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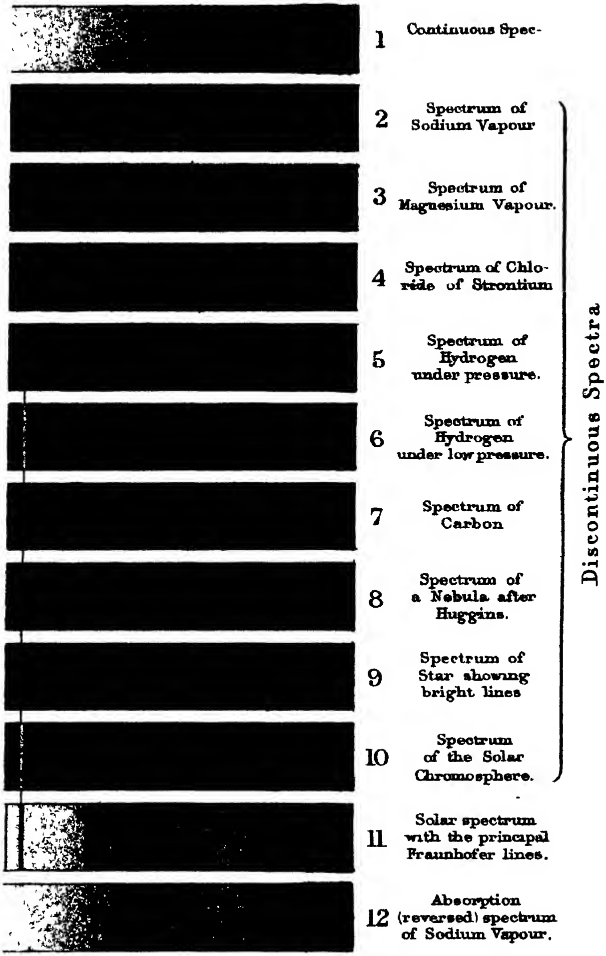

ı blue, blue and dark blue are the lines of incandescent hydrogen, the two
ndescent sodium vapour · the long line in the yellow. D_3 (Helium?) does not
l with the lines of any known terrestrial substance; the 3 lines of unequal
gnesium. Compare this spectrum with certain absorption lines in No. 11.
andescent sodium vapour in No. 2 appear dark when the continuous spec
light passes through sodium vapour.

F S.Weller, lith.

INORGANIC CHEMISTRY

THEORETICAL AND PRACTICAL

A Manual for Students in Advanced Classes

BY

WILLIAM JAGO, F.C.S., F.I.C.

SECOND EDITION

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PREFACE

One of the established facts in connection with the teaching of Science in this country, is the formation of classes in every part of the kingdom under the auspices of the Science and Art Department. The functions of this body are not confined to its own classes, for it also receives a wide recognition as an Examining Board. With the existence of such class teaching and examinations, it becomes an imperative necessity that teachers and students shall model their work on the lines of general treatment adopted by the Department in various subjects.

As its name implies, the present work is the result of an endeavour to meet the requirements of students in the Department's 'Advanced' Chemistry Classes. There are two ways in which such a text-book may be prepared; it may either be simply an examination cram-book, or it may aim at supplying the materials for such a bona-fide course of study as that the skeleton of which is given in the syllabus of the Department. It is respectfully submitted that a work may be so shaped as to fulfil these conditions and still be a genuine text-book of chemistry. On the principle that 'the greater includes the less,' a text-book satisfying the requirements of the syllabus will also satisfy those of the examination.

The planning of this work has been a matter of some little difficulty, because such students as those for whom it is espe-

cially prepared have already some knowledge of chemistry. In the elementary classes they will have acquired a familiarity with certain elements, and a few of their more important compounds. In the advanced classes not only must a greater number of elements be treated, but also those previously studied must be dealt with more completely and the general laws of chemistry more fully and exhaustively examined. For the sake of continuity this work has been begun at the commencement of the science, but throughout it is assumed that the reader has such knowledge as is conveyed by the author's Elementary Text-Book on the same subject. Therefore, such matters as are explained very fully in the elementary book are here treated more scantily, and instead, other information concerning the same elements is given. For example, the experimental modes of preparing and testing the various elements (dealt with very fully in the elementary work) are here largely replaced by descriptions of their manufacture and industrial applications. The plan of the book is such as I have found to answer well in my own teaching of such classes; I therefore venture to hope it will commend itself to other teachers.

Certain portions of the Elementary Text-Book have so recently been re-written that I have adopted them in this work almost without change, and that, first, for the reason that I felt that in my hands, at least, any attempt at altering, for the sake of altering, would not be an improvement. Further, I consider that if by similarity of expression and treatment the work of the elementary course can be welded on to that of the advanced without abrupt change, a decided advantage to the pupil is thereby gained.

Having recently written a short treatise on analysis for Science class students, I have not thought it necessary to add to the bulk of this work by including descriptions of analytic methods.

I have not hesitated to take extensive advantage of the classic works on various departments of chemistry of Miller, and Meyer, placed at my disposal by Messrs. Longmans & Co. My acknowledgments are also due to the journals of the Chemical Society, and standard treatises by Roscoe and others.

Hoping, as I venture to do, that this work may receive from teachers some at least of the favourable recognition accorded to my previous efforts, I beg to say that any suggestions from them as to its improvement will be warmly welcomed, and shall be most carefully considered, when, thanks to their appreciation, a future edition of the book is required.

WILLIAM JAGO.

BRIGHTON: July, 1890.

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PLATE

EMISSION AND ABSORPTION SPECTRA . . . *Frontispiece*

TEXT-BOOK

OF

INORGANIC CHEMISTRY

CHAPTER I

INTRODUCTORY

1. **Matter.**—There is an almost endless diversity among

The table of Emission and Absorption Spectra is inserted by the kind permission of Mr. Norman Lockyer.

is convenient to have one name that shall include all such bodies; for this purpose the Germans use the word literally translated by 'stuff'; in English we employ the term *matter*. **Matter, then, is anything which possesses weight (i.e. is acted on by gravitation), and exists in three distinct forms, namely, as solids, liquids, and gases.**

2. **Force.**—It would, at first sight, seem that the definition of matter just given is sufficiently extensive to embrace everything, but yet a moment's consideration will show that there are other things beside matter. To give an illustration: you

know that a hammer-head consists of matter because it possesses weight, but if with this hammer you give a series of blows to a small piece of nail rod, you have given something which is not matter. The hammer-head is not lighter, neither is the piece of nail rod heavier. Still the blows are something, as otherwise they could produce no effect. For one thing the piece of nail rod will have been flattened and altered in shape; further, and of more importance to us at this moment, it will have become hot to the touch. Again, to mention another example, if a brick be most carefully weighed, and then made red-hot in a furnace, the hot brick weighs precisely the same as it did when cold. Further, if it be allowed to cool, this hot brick imparts heat to surrounding objects, and nevertheless remains unaltered in weight. Here, then, we have something very definite, which a body can receive and again yield, and which is not matter. Let us try to see what relationship this something has to matter; in the first illustration, the blows were struck by the moving hammer-head, which consists of matter in motion The more rapid the motion, the more violent would be the blows; in fact the force of the blow depends both on the quantity of matter and the rapidity of its motion. Further, although outside any attempt at present proof, the hot iron of the nail rod, and also the hot brick differ from the same substances in the cold state, in that their component particles are in a state of movement; as these substances cool, the particles once more enter into a condition of comparative rest. This something, then, beyond matter is closely associated with motion, and is termed force. **Force is defined as that which is capable of setting matter in motion, or of altering the direction or velocity of matter already in motion.** The motion of bodies may be divided into two classes: there is first that of the body as a whole, as in the case of the moving hammer-head; 2nd, the internal movement of the particles of a body, as when it becomes hot.

3. Object of Chemistry.—It is now easy to explain the objects of chemistry. Matter is not only most varied in form,

but its form is also continually varying; it is the function of the chemist to investigate these changes, and also the nature of the substances which participate in them. In short, **chemistry is that science which treats of the composition of matter, of the changes produced therein by heat and other natural forces, and of the action and reaction of different kinds of matter on each other.**

4. **Chemical as distinguished from Physical Changes.**—It is necessary to learn to distinguish between what are simply alterations in the physical properties of matter, and what are really chemical changes. Thus to give an illustration, if a piece of platinum wire be heated in a bunsen flame it immediately becomes white-hot, but on being removed once more cools and regains its original brightness; no alteration in the wire has been caused by the act of thus heating, it is not even tarnished. If a piece of iron wire be similarly treated, a slight tarnish is produced on the outer surface, but otherwise there is little alteration. On heating in the same manner a piece of magnesium wire, it immediately on becoming hot bursts into flame and burns with a dazzling white light, depositing a white, friable (easily powdered) body, composed of magnesium and another substance called oxygen, and to which the name of magnesia has been given. In the case of the platinum, the change produced is merely physical, and although the hot wire possesses properties which are absent in the cold, yet on the wire losing its heat it again regains its previous characters. With the iron wire there is a slight superficial change, for the iron, like the magnesium, is capable of combining with oxygen, but has only done so to a limited extent on the surface: the interior and main portion of the wire is unaltered. But in the third instance there has been a vigorous chemical change, the whole of the magnesium has disappeared as such, and its place is occupied by the new body magnesia. Again, let a current from an electric battery be passed through a piece of copper wire, the wire to all appearance is unaltered, but if it be dipped in iron filings the little

fragments cling to it as though it were a steel magnet. On ceasing the electric current the magnetic action ceases, to be again resumed if the current is once more passed. This is again a physical change, produced this time by electricity. But supposing, instead of passing the current through a copper wire, it is passed through some slightly acidulated water, gaseous bubbles of an explosive nature are evolved; in this case a chemical change has been effected. Experiments, such as these, teach that **chemical changes are distinguished from those of a merely physical character by more or less striking permanent alterations in the appearance and properties of the substances involved therein.** As instances we may cite changes of colour, as when potassium iodide and mercury chloride, both colourless bodies, produce by their action on each other the bright orange-red iodide of mercury. There are changes in smell, as when quicklime acts on ammonium chloride and causes the evolution of ammonia, with its characteristic pungent odour. There are changes in taste, as when by chemical action either starch or cotton-wool is transformed into sugar. Many more examples might be given, but with these the student will become familiar as he proceeds with his studies. It will suffice at present to mention in addition, that chemical action is often accompanied by changes from one of the physical states of matter to another. Thus liquids may become solids, and solids liquids or even gases. An exceedingly familiar illustration of this latter is that of the burning of an ordinary candle. To all appearance the candle itself vanishes and is completely lost, nevertheless it is very easy to trace its components after the candle has disappeared. If it be burned in a closed vessel of air, the flame soon goes out, and the air on examination is found to possess properties distinctly different from those by which it was previously characterised. Before the experiment, if the air had been shaken up with a solution of lime in water (which is a perfectly clear liquid), the liquid would have remained clear. But afterwards on thus shaking the two together, the lime-water becomes milky. The reason of this is that a candle is composed largely of two substances called carbon and hydrogen;

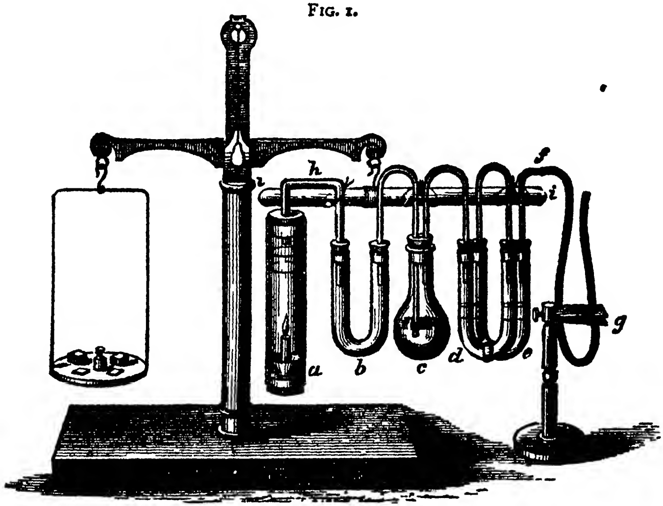
the air contains a substance called oxygen. When the candle burns, its carbon combines with the oxygen of the air, and produces a new body, called carbon dioxide; this is distinguished by the property of turning lime-water milky. Further, the hydrogen of the candle also combines with oxygen, and in so doing produces a body called water; this too can be detected as one of the substances into which the candle is changed. It will be seen, then, that although the candle in the act of burning disappears, yet the bodies of which it is composed are not destroyed, for by appropriate means they can be recognised and, if wished, recovered.

5. **Indestructibility of Matter.**—Although chemical action can produce such marvellous changes, yet there is one thing it cannot do—it can neither create nor destroy matter. An illustration of this latter point is afforded by the burning candle described in the last paragraph; but the same experiment, when performed under more exact conditions, shows not merely that the products of the burning candle can be traced, but also that they more than fully equal in weight the original candle itself. The apparatus necessary for this purpose is shown in fig. 1.

In this apparatus the candle is placed inside a glass chimney, *a*, such as is used for Argand lamps. At the lower end is a cork, through which have been bored some three or four holes for the admission of air. By means of corks and pieces of bent glass tubing *a* is attached to the vessels *b*, *c*, *d*, *e*, all of which, except the flask *c*, are bent tubes termed by the chemist U-tubes. The first tube, *b*, is empty, the flask *c* contains lime-water, a tube from *b* reaching down beneath its surface. In *d* and *e* are placed fragments of either potash or soda, while the exit-tube at *f* has attached to it a piece of india-rubber tubing held in the clamp *g*. The whole series, *a*, *b*, *c*, *d*, *e*, are fastened to a rod *i i*, which in its turn is suspended from the arm of a balance, and then accurately counterpoised by weights placed in the opposite scale-pan. The tube *g* is connected to a pump or some other appliance, by which a current of air can be drawn through the whole apparatus. The candle is taken

out, lighted, immediately replaced, and the current of air set going. As the candle burns, the water produced condenses in *b*, and is at once recognised, the carbon dioxide turns the

Fig. 1.

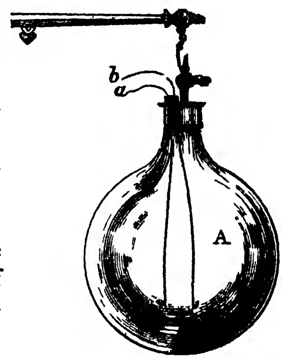


lime-water in *c* milky, while in *d* and *e* any small quantities of water and carbon dioxide which have escaped so far are arrested by the potash or soda, either of which readily absorbs and retains both these bodies. As the experiment proceeds the apparatus increases in weight, and that side of the balance gradually descends. In this way proof is obtained of the fact that the products of combustion weigh more than the original substance burned, the increase being due to the oxygen with which the substance has combined. This experiment, although striking, is incomplete, because no account has been taken of the weight of the oxygen before its combination with the candle. Our knowledge thus obtained is supplemented by the following experiment.

The apparatus shown in fig. 2 consists of a glass flask of some 250 cubic inches (4 litres) capacity, fitted with a stop-cock, and two wires *a*, *b*, passing through the cork and con-

nected at the lower ends by a piece of fine platinum wire. Around this wire a piece of gun-cotton, weighing about 10 or 12 grains, is lightly wrapped, and then introduced into the flask. By means of an air-pump the flask is completely exhausted and then weighed. On passing an electric current through *a*, *b*, the platinum wire becomes red-hot and ignites the gun-cotton, which completely disappears, with a bright flash. On again weighing the flask it will be found to remain unaltered in weight. As a result of being heated the gun-cotton has undergone a chemical change by which it has been converted into gases; these, however, weigh precisely the same as did the original gun-cotton. The result of this and all other similar experiments is summarised in the statement that **matter is indestructible, and consequently the same weight of material remains after any and every chemical change as there was before its commencement.**

FIG. 2.



6. Mechanical Mixture and Chemical Combination.—It is important to learn to distinguish between these two different processes, and this end is best attained by the study of a typical experiment. If some sulphur be obtained in the form of a fine powder it is of a brilliant yellow colour, while copper reduced to the state of filings is of a red tint. In general properties the sulphur is extremely brittle, while the copper is marked by great toughness. These two powders may be mixed together in any proportion, with the production of a greenish-yellow mass, the yellow being more or less pronounced according to the quantity of sulphur present. If the copper and sulphur be in a sufficiently fine state of powder the mixture shows to the naked eye no signs of the presence of individual particles of either sulphur or copper; still, under a

sufficiently powerful microscope the separate fragments of each may be perceived lying side by side. It is thus possible to *see* that no actual union has occurred; further, the properties of the mixture are just a mean of those of the ingredients. In addition, the two bodies are readily separated from each other. If the mixture be transferred to a test-tube and shaken with water, the sulphur being much the lighter remains suspended in the water sufficiently long for the copper to settle to the bottom as an approximately pure layer. The water being poured off, and the washing once or twice repeated, the copper is regained in a state of purity. Or, as an alternative method, the sulphur may be removed by dissolving it in a liquid called carbon disulphide, which does not dissolve copper. But if this mixture of copper and sulphur be placed in a dry test-tube and then gently heated at the lower end, the sulphur is first seen to melt, and then the contents of the tube commence to glow at the bottom with a gentle red heat; the tube may now be removed from the flame, and the glow will spread throughout the whole mass. On now allowing the tube to cool a bluish-black mass remains, which is very brittle and totally unlike either the copper or sulphur in appearance. The microscope enables us to distinguish no separate particles of either copper or sulphur; no washing processes enable us to again separate these two bodies from each other. Definite chemical union between the two has occurred, and if the resultant body, named copper sulphide, is examined it is found to contain copper and sulphur in certain fixed and invariable proportions. It is well to have an excess of sulphur in the mixture prior to the act of heating; that excess is then driven off in the form of vapour, leaving behind simply the quantity necessary to form the copper sulphide.

7. Element, Compound, Mixture.—Before proceeding further it will be well to have definitions of these terms; they are therefore appended :—

An Element is a substance which has not been separated into two or more dissimilar substances.

A Compound is a body produced by the union of

two or more elements in definite proportions, and consequently is a substance which can be separated into two or more dissimilar bodies. Compounds differ in appearance and characteristics from their constituent elements.

The term Mixture is applied to a substance produced by the mere blending of two or more bodies, elements or compounds, in any proportion without union. Each component of a mixture still retains its own individuality and properties, and separation may be effected by mechanical means.

8. List of Elements.—Although the number of different substances observed around us is practically infinite, yet there are comparatively few elements. Practically, all natural bodies are mixtures either of elements or compounds; in many of the mixtures, however, one element or compound largely predominates, while in a few cases the element or compound is found in a condition of almost absolute purity. On investigation these natural mixtures and compounds are found to be capable of resolution into elements, and although the compounds are so diverse in character, yet it is estimated that nine hundred and ninety-seven thousandths of the earth's crust is composed of only nine elements. In addition to these nine very plentiful elements, there are about thirty that may be termed common, while the remainder of the list, given in the subjoined table, are rare or very rare. It should be noticed that our definition of an element is a somewhat tentative one; it is not said that an element is a body which *cannot* be separated into dissimilar substances, but a body which *has not.* The accepted list of elements has undergone some curious vicissitudes. With the advance of chemical science certain bodies at one time supposed to be elements have been discovered to be compounds, and as more substances have been subjected to chemical research and by more refined and powerful modes of examination, a number of elements existing in only minute quantities have been added to the list. One of the most striking examples of the discovery of the com-

pound nature of supposed elements was that of the decomposition by Sir Humphrey Davy of potash and soda, previously ranked as elementary bodies, into the metals potassium and sodium, and oxygen and hydrogen. It may be fairly assumed *that as investigation* continues new elements will be discovered, *although most probably in exceedingly* minute quantities. *Reference is subsequently made to recent examination of some of the bodies at present in the Elementary List.*

TABLE OF ELEMENTS

Name	Symbol	Atomicity or Valency	Combining or Atomic Weight
Aluminium	Al	IV	27·1
Antimony (Stibium)	Sb	V	120·2
Arsenic	As	V	75
Barium	Ba	II	137
Beryllium	Be	II	9·1
Bismuth	Bi	V	208
BORON	B	III	11
BROMINE	Br	I	80
Cadmium	Cd	II	112
Cæsium	Cs	I	132·9
Calcium	Ca	II	40·1
CARBON	C	IV	12
Cerium	Ce	III	140·3
CHLORINE	Cl	I	35·37
Chromium	Cr	VI	52·2
Cobalt	Co	IV	59
Copper (Cuprum)	Cu	II	63·4
Didymium	Di	III	146
Erbium	Er		166
FLUORINE	F	I	19
Gallium	Ga		69·8
Germanium	Ge		72·3
Gold (Aurum)	Au	III	196·6
HYDROGEN	H	I	1
Indium	In	III	113·7
IODINE	I	I	126·6
Iridium	Ir	IV	193
Iron (Ferrum)	Fe	VI	56
Lanthanum	La	III	139
Lead (Plumbum)	Pb	IV	206·5

Table of Elements

Name	Symbol	Atomicity or Valency	Combining or Atomic Weight
Lithium	Li	I	7
Magnesium	Mg	II	24
Manganese	Mn	VI	54·8
Mercury (Hydrargyrum)	Hg	II	200
Molybdenum	Mo	VI	96
Nickel	Ni	IV	58·5
Niobium	*Nb*	V	94
NITROGEN	N	V	14·1
Osmium	Os	VI	199
OXYGEN	O	II	16
Palladium	Pd	IV	106
PHOSPHORUS	P	V	31
Platinum	Pt	IV	194·8
Potassium (Kalium)	K	I	39·1
Rhodium	Rh	IV	104
Rubidium	Rb	I	85·4
Ruthenium	Ru	VI	104
Samarium	Sm		150
Scandium	Sc	III	44
SELENIUM	Se	VI	79
SILICON	Si	IV	28·3
Silver (Argentum)	Ag	I	108
Sodium (Natrium)	Na	I	23·1
Strontium	Sr	II	87·5
SULPHUR	S	VI	32·1
Tantalum	Ta	V	182
TELLURIUM	Te	VI	126
Terbium	Tr		148
Thallium	Tl	III	204
Thorium	Th	IV	232·5
Tin (Stannum)	Sn	IV	118
Titanium	Ti	IV	48·2
Tungsten (*Wolfram*)	W	VI	184
Uranium	U	VI	240
Vanadium	V	V	51·3
Ytterbium	Yb	III	173
Yttrium	Y	III	89
Zinc	Zn	II	65
Zirconium	Zr	IV	90

The columns in the foregoing table, headed respectively,

Symbol, Atomicity, and Combining Weight, will receive explanation in later parts of this work.

9. Metals and Non-Metals.—The elements have been divided into two groups, according to whether they are metallic or non-metallic in their nature. The metallic properties are very decided in a metal such as either iron, copper, or gold; and equally it is obvious that such bodies as sulphur and phosphorus are not metals. But although the properties of these are very definite, a number of other bodies are much less marked in character; in fact there is no well-defined line of division between the two classes, as the one series gradually merges into the other. Thus the element arsenic, which occupies an intermediate position, is placed by some chemists among the metals, and by others among the non-metals. In physical character the metals are, in mass, opaque bodies, having a peculiar lustre termed metallic; they are comparatively good conductors of heat and electricity. These properties do not exclusively belong to the metals, for carbon in the form of graphite has a very decided metallic lustre, and conducts electricity well. Chemically, the metals as a whole form oxides which act as bases, while the non-metallic oxides form acids, but even in this respect the two series overlap each other. The non-metals in the table just given are indicated by being printed in small capitals; the common metals are printed in ordinary type, and the rarer metals in italics.

At ordinary temperatures two of the elements—mercury and bromine—are liquid; four—hydrogen, chlorine, oxygen, and nitrogen—are gaseous, but can be liquefied by intense cold and pressure. The remaining elements are solid, but at varying temperatures have been liquefied, with the exception of carbon, which so far has only been slightly softened with the highest temperatures at our command.

10. Composition of the Earth's Crust.—From analysis of various samples of rock and rock-forming materials, it has been estimated that the earth's crust has the following approximate composition:—

Oxygen	480
Silicon	290
Aluminium	80
Iron	60
Calcium	30
Magnesium	20
Sodium	20
Potassium	15
Hydrogen	2
Other elements	3
	1000

11. Modes of Chemical Action.—Although chemical actions vary greatly in character, they may be all classified under the following five heads.

I. Direct Union, or Synthesis.—The word synthesis means a putting together, and the operation is termed synthesis when new compounds are built up by the combination of elements, or by the combination of simpler to form more complex compounds. The simplest type of synthesis is that of direct union of the bodies ; of this we have examples in the combination of magnesium and oxygen to form magnesia, sulphur and copper to form copper sulphide, and many others.

II. Displacement.—The various elements possess different degrees of chemical activity ; thus some, such as magnesium, enter into combination with other elements with great readiness ; others, as platinum, form comparatively few compounds. In consequence of such differences in activity some elements are able to displace others from compounds already formed. Thus iron is a more active element than copper, and if a piece of iron be placed in a solution of a compound of copper and chlorine, the iron displaces the copper ; a compound of iron and chlorine is formed, and copper is liberated in the free state. Again, chlorine is a more active element than oxygen, and if water, a compound of oxygen and hydrogen, be submitted to the action of chlorine, the latter element displaces the oxygen, and a compound of chlorine and hydrogen is formed.

III. Mutual Exchange.—When two or more compounds are brought together, there are sometimes conditions which lead to an exchange between them of their various constituent

elements. Thus, if solutions of mercury chloride (a compound of mercury and chlorine) and potassium iodide (a compound of potassium and iodine) be mixed together, the mercury and iodine, through mutual attraction, unite to form a new compound—mercury iodide. So, too, the remaining elements, potassium and chlorine, also unite to form a new compound, potassium chloride. Putting it in other words, the mercury has under these conditions a greater attraction for iodine than for chlorine, and consequently the mercury takes the iodine, and hands over the chlorine to the potassium. The causes which determine such interchanges will receive subsequent examination.

IV. Re-arrangement of Particles.—This class of chemical action belongs almost exclusively to the domain of organic chemistry. There are many examples of compounds in which, without altering the proportions of each element present, fresh compounds may be formed by changing the arrangement of the particles within the compound. Such changes may be compared to those in which the same letters by transposition may be caused to form two distinct words.

V. Direct Decomposition, or Analysis.—This type of chemical action is just the exact opposite of the first mentioned, and consists of the breaking up of a compound either into simpler compounds or elements. The word analysis means a separating or taking apart. A very striking example of analysis is that of heating the compound termed mercury oxide, and thus separating it into gaseous oxygen and liquid metallic mercury.

As stated, the first and last of this series of modes of chemical action are the one an example of direct synthesis, and the other of direct analysis; in chemical action by mutual exchange, both analysis and synthesis occur. First, the compounds are separated into their constituent elements, and then these elements combine, and by synthesis produce the new compounds. It is frequently much more convenient to prepare a compound by this indirect method of synthesis rather than by direct union of its constituent elements.

12. Relation of Chemical Action to Heat.—Whenever chemical combination occurs heat is evolved as one of

the results. This is seen very strikingly in such everyday chemical actions as the burning of a fire, or in the quenching of lime. The bricklayer takes quicklime, and, as a preliminary step to the making of mortar, adds water to the lime; the two combine to produce, if no excess of water is used, a dry powder consisting of slaked lime. In this act of combination, heat is liberated in considerable quantities. Let it be remembered that **chemical combination is invariably accompanied by the production of heat, and this production of heat is one of the best proofs of the occurrence of chemical combination.** On the other hand, in order to separate a compound into its elements heat is necessary and disappears as such, being stored up in the elements in such a way as to be again liberated on their re-combination. In chemical action by displacement or mutual exchange, there is both absorption and liberation of heat; because first the compound bodies are decomposed, and then new combinations are effected. Usually in such cases the heat of combination is more than that absorbed by decomposition. There are a few apparent exceptions to the first statement made, as when hydrogen and iodine combine; but in these cases it will be found that decompositions as well as combinations have occurred, and the former action has absorbed more heat than is liberated by the latter.

13. Contact necessary for Chemical Action.—The whole of the various modes of chemical action are combination, decomposition, or interchange of particles of matter; from the very nature of such changes it is necessary that the bodies participating be in actual contact. Thus, we know that under the influence of heat copper and sulphur combine, with vigorous chemical action; but if they are separated by an interval of space, combination is obviously impossible. Of necessity, then, we lay down the law that **chemical action can only occur between bodies actually in contact.** In illustration of this point, potassium chlorate and sugar may be mixed together, and then touched with a glass rod moistened with concentrated sulphuric acid; vigorous combustion immediately occurs, but

while the two are separated by an interval, however small, no action whatever ensues.

In order that chemical action once commenced shall continue, it is necessary that means be provided for removing the products of such action as rapidly as formed, so that fresh portions of the substances may be brought into contact. The requisite mobility of particles necessary for this is best obtained by having one at least of the bodies in the liquid state. Either the bodies may, for this purpose, be dissolved in some suitable medium, or they may be liquefied by fusion.

In the matter of contact, chemical action apparently differs from heat and electricity as examples of other natural forces. Thus heat acts over great distances, as when the sun imparts heat to bodies on the earth; a glowing mass of red-hot iron will melt and inflame a piece of phosphorus placed some inches from it. So, too, an electrified glass rod attracts a pith ball held a considerable distance away. The difference, however, is apparent rather than real, for these forces only act at a distance by means of a medium which fills the space between the two objects and thus produces continuity. The pull of a steam-engine may act on a mass of matter at some distance, because they are connected by a rope. Between the sun and the earth there is a medium by which the force of heat acts, which is just as real, though not so tangible, as the rope between a steam-engine and the bucket of ore it may be raising from the depths of a mine.

14. Heat Measurements.—Chemical action and heat are so materially dependent on each other that it becomes necessary for the chemical student to be familiar with the most important measures of heat.

15. Temperature.—The commonest heat-measure we have is that which we gain by means of the sensation of warmth it produces. According to the character of this sensation a body is said to be cold, warm, or hot. These terms all refer to the power which the body has of communicating heat to other bodies. The measure of this power is termed temperature, which is more exactly embodied in the following

definition :—**The temperature of a body is a measure of the intensity of its heat, and is further defined as the thermal state of a body considered with reference to its power of communicating heat to other bodies.**

16. The Thermometer.—For scientific purposes the sensations are not sufficiently accurate methods of measuring temperature; accordingly temperature is usually measured by certain of the effects which heat produces. Among these one of the most convenient is that most bodies expand with an elevation of temperature. This expansion is distinctly perceptible with solids, occurs to a greater extent in liquids, and most of all with gases. For the general purposes of temperature-measurement, the metal mercury is the most convenient substance. This liquid, enclosed in a suitable vessel, constitutes the temperature-measuring instrument termed a thermometer. In constructing a thermometer, a bulb is blown at one end of a glass tube of very narrow bore; the bulb and a portion of this tube are next filled with carefully purified mercury; this is boiled and thus all air and moisture are driven out of the tube; the open end is then hermetically sealed, by fusing the glass itself. One then has the bulb and a portion of the tube filled with mercury, and the remainder of the tube a vacuum, save for the presence of a minute quantity of mercury vapour. On heating the bulb of this instrument the mercury expands and rises considerably in the stem. Throughout any body or series of bodies, heat has a tendency to so distribute itself that the whole series shall be at the same temperature, consequently if the thermometer be placed in contact with the body whose temperature it is desired to measure, a redistribution of heat occurs, until the two are at the same temperature. That is to say, if the body be the hotter it receives heat from the thermometer, and if it be colder it yields heat to the thermometer until the temperature of the two is the same. The two being in efficient contact, this stage is indicated by the mercury becoming stationary in the thermometer. Now the volume of mercury is constant for any one temperature; therefore, to register temperature, it is only necessary to have further a scale or

series of graduations attached to the stem of the instrument, by which the temperature may always be read.

17. Thermometric Scales.—In graduating thermometers, two fixed points of temperature are almost universally employed : these are the temperatures of melting ice, and of the steam from boiling water. Certain simple precautions being taken, these temperatures are always constant. It is, in addition, necessary to graduate the thermometers, so as to register temperatures intermediate between these two points, and also below and above them. The most convenient system of graduation is that of Celsius, known also as the centigrade scale. In this scale the distance between the melting-point of ice (or the freezing-point of water, as it is commonly termed) and the temperature of steam at ordinary pressure is divided into 100 equal graduations or degrees. (This latter temperature is more commonly described as being that of the boiling-point of water.) The freezing-point is called zero, or 0°, and the boiling-point 100°. Degrees of the same value are set out above and below the boiling and freezing points : the temperatures below 0° are reckoned in − degrees, counting downwards; thus 10 degrees below the freezing-point is −10°, and so on. Degrees above the boiling-point simply count upwards; thus 10 degrees above the boiling-point is 110°, and so on, to as high temperatures as have been measured. This scale is exceedingly convenient, and is that most largely used by scientific men in all countries; it is also the scale adopted for general use in France. In England the scale known as that of Fahrenheit is commonly adopted : the distance between the freezing and boiling points is divided into 180 equal parts, and degrees of the same dimensions set out above and below the boiling and freezing points. Fahrenheit assumed that the greatest cold attainable was 32 degrees below the freezing-point, and accordingly took that point as his zero and reckoned from it upwards. The freezing-point thus became 32° F., and the boiling point $32+180=212°$ F. Degrees below the Fahrenheit zero reckon downwards as minus degrees. In Germany and Russia temperature is reckoned on the Réamur scale, in

which the freezing-point is 0° and the boiling-point 80°. It is frequently necessary to be able to compare these scales and to translate temperatures from any one into another. The following comparative values of the degrees of each scale will be of assistance to the student in doing this:—

1 Centigrade degree	.	.	$=\frac{9}{5}$ Fahrenheit degree.
1 ,, ,,	.	.	$=\frac{4}{5}$ Réamur ,,
1 Fahrenheit ,,	.	.	$=\frac{5}{9}$ Centigrade ,,
1 ,, ,,	.	.	$=\frac{4}{9}$ Réamur ,,
1 Réamur ,,	.	.	$=\frac{5}{4}$ Centigrade ,,
1 ,, ,,	.	.	$=\frac{9}{4}$ Fahrenheit ,,

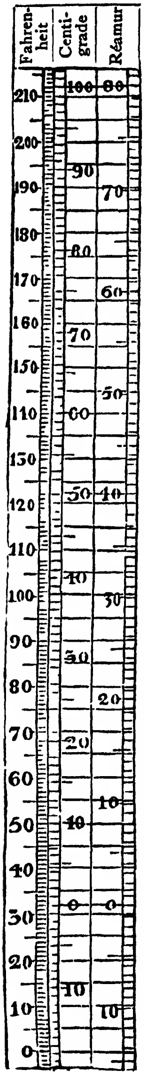
Conversions from centigrade to Réamur, and *vice versâ*, are very simple, because the zero of the two scales coincide. So, too, it is easy to convert any number of degrees centigrade into the equivalent number of Fahrenheit degrees above the freezing-point; but after this is done provision must be made for the difference of the zeros. The same holds good for the converse operation. The following formulæ show how temperatures on the one scale may be converted into those of another:—

Centigrade to Fahrenheit .	$\frac{C.^\circ \times 9}{5} + 32 = F.^\circ$
,, ,, Réamur . . .	$\frac{C.^\circ \times 4}{5} = R.^\circ$
Fahrenheit ,, Centigrade .	$\frac{(F.^\circ - 32) \times 5}{9} = C.^\circ$
,, ,, Réamur . .	$\frac{(F.^\circ - 32) \times 4}{9} = R.^\circ$
Réamur ,, Centigrade . .	$\frac{R.^\circ \times 5}{4} = C.^\circ$
,, ,, Fahrenheit .	$\frac{R.^\circ \times 9}{4} + 32 = F.^\circ$

The accompanying figure (No. 3) exhibits the three scales side by side, and shows the number of degrees on each for one and the same temperature.

18. Quantity of Heat.—Temperature is not a measure of quantity of heat, for a thermometer would indicate the same temperature both in a vessel containing a pint, and one containing a gallon, of boiling water, although it is

FIG. 3.



evident that the one must contain eight times as much heat as the other; further, to raise the gallon of water to the boiling-point, eight times the amount of heat necessary to similarly raise the pint is required. This leads us to the mode of measuring and indicating *quantity* of heat. **Quantity of heat is measured by the amount necessary to raise a certain weight of some body from one to another fixed temperature. The quantity of heat necessary to raise 1 gram of water from 0° to 1° C. is termed a Unit of Heat.**

The quantity of heat necessary to raise different substances through one degree of temperature varies very considerably. **The quantity of heat necessary to raise 1 gram of any substance through 1 degree of temperature is termed its Specific Heat.** From this definition it follows that the specific heat of water at 0° C. is unity.

19. **Symbols and Formulæ.**—For convenience of description, **each element has an abbreviation of its full name, called its symbol.** These abbreviations consist, where practicable, of the initial letter of the Latin name of the element. As, however, there are nearly seventy elements, and only twenty-six letters in the alphabet, a large number of the symbols are composed of the initial and another distinctive letter selected from the name. Thus, the three elements carbon, chlorine, and copper (cuprum), all have names commencing with 'C;' carbon, being the most important element, has the letter C for its symbol, while Cl and Cu are written respectively for chlorine and copper. The symbols are given in the Table of Elements, contained in the eighth paragraph.

As all compound bodies are the result of the union of elements, they may be conveniently expressed symbolically by placing side by side the symbols of the constituent elements. **The symbol of a compound is termed its formula.** Thus common salt consists of sodium and chlorine, and NaCl is accordingly written for its formula.

20. Further Uses of Symbols and Formulæ; Law of Chemical Combination by Weight.—Simply as abbreviations of the full names, symbols and formulæ are of great service; this, however, is but a small part of their significance and value in chemistry. In order to explain their further use, reference must be made to certain information gained by experiment, careful attention to which is directed. The following table gives the combination by weight of a number of compounds, as obtained by most careful analysis :—

Name of Compound	Composition	
Hydrochloric acid . .	1·0 of hydrogen,	35·37 of chlorine.
Sodium chloride . .	23·1 ,, sodium,	35·37 ,, ,,
Silver ,, . .	108·0 ,, silver,	35·37 ,, ,,
Water	2·0 ,, hydrogen,	15·96 ,, oxygen.
Silver oxide . . .	216·0 ,, silver,	15·96 ,, ,,
Copper chloride . .	63·4 ,, copper,	70·74 ,, chlorine.
,, oxide . .	63·4 ,, ,,	15·96 ,, oxygen.

Examination of this table shows that the quantity of each element present in each compound is either a particular number, or multiple of that number. The more extended the list of compounds subjected to examination, the more striking is the evidence that each element has a certain unit-quantity of combination of definite weight. **It is possible to assign to every element a number, which number, or its multiple, shall represent the proportionate quantity by weight of that element which enters into any chemical compound. These numbers are termed the combining or atomic weights of the elements, and are deduced from results obtained on actual analysis.** In addition to its use as an abbreviated title of any element, **the symbol represents the quantity of the element indicated by its combining weight.**

When compounds contain multiples of the combining weight of any element the fact is indicated by placing a small figure after the symbol and slightly below the line. The large figures at times used before a symbol or formula apply to the whole of the symbol or formula which follows. The combining weights are given in the table of the elements in the eighth paragraph.

In hydrochloric acid the weights of hydrogen and chlorine respectively are the same as those given in the table of combining weights; therefore, the symbol is HCl, which indicates that that body has been found to consist of 1 by weight of hydrogen, and 35·37 of chlorine. Sodium chloride and silver chloride are in the same category, and accordingly have respectively the formulæ NaCl and AgCl. Water combines twice the combining weight of hydrogen to one combining weight of oxygen; this is expressed in the formula by writing H_2O. Similarly, silver oxide contains twice the combining weight of silver, and has the formula Ag_2O. Copper chloride contains twice the combining weight of chlorine, and has consequently the formula $CuCl_2$; copper oxide has, however, simply one combining weight each of copper and oxygen, and has CuO as its formula. **The quantity of an element represented by its combining weight may be termed 'one combining proportion' of that element.** A word of caution may not be here out of place as to the views with which tables of combining weights are regarded. These tables embody the conclusions to which chemists as a whole have arrived as the result of exhaustive experiment; but important alterations have in the past been made in such tables, and may have again to be made. Further, the young student especially must avoid getting into the train of reasoning that because hydrogen and chlorine, for instance, have as combining weights the numbers 1 and 35·37, therefore they unite in these proportions. The true course of reasoning is that experiment has shown that they combine in such proportions, and therefore those numbers have been given them as their combining weights.

21. Atoms and Molecules.—The fact that the quantity of every element which enters into combination is either a

certain definite and unchangeable weight, or a multiple of that weight, has caused chemists to feel that this weight of a combining proportion of an element is in some way associated with its physical nature. This view is strengthened by the fact that throughout the whole series of known compounds each element invariably obeys this law. Chemists are therefore led to assume a unit of chemical combination, and to this they have given the name of 'atom,' a word which signifies that which is indivisible. For chemical purposes, **An atom may be defined as the unit quantity of chemical combination of each element, and is the smallest quantity of any element which has been caused to enter into, or to be expelled from, a chemical compound.** For the phrase 'combining proportion,' the term 'atom' may be substituted. **The combining weight is thus the relative weight of the atom of each element compared with that of hydrogen, which, being the lightest, is taken as unity.**

The little group of atoms represented by the formula of a compound is termed a 'molecule.' **A molecule is the smallest possible particle of a substance which is capable of separate existence.** No subdivision of molecules of chemical compounds is possible without the decomposition of such compounds either into the atoms of the constituent elements, or into two or more molecules of some simpler chemical compound or compounds.

22. **Elementary Molecules.**—The definition just given of molecules applies not only to compounds, but also to elementary bodies. **The elements in the free or uncombined state exist in the form of molecules, such molecules in most cases consisting of two or more atoms united together.** The number of atoms present in the molecule of an element, is shown by a small figure after the symbol; thus a molecule of oxygen, containing two atoms, is represented by O_2. When in any case it is desired to express symbolically a number of atoms of an element, this must be done by the use of a large figure before the symbol; thus 2O or 3O means simply two or three atoms of oxygen, but O_2 or

O_3 would mean that the molecule contained either two or three atoms of oxygen as the case might be.

The whole atomic and molecular theory will subsequently receive more ample description and explanation.

23. Chemical Equations.—Chemical changes are most conveniently expressed by what are termed 'chemical equations;' these consist of the symbols and formulæ of the bodies participating placed before the sign =, while those of the resulting bodies follow.

As an example, the following equation represents the chemical action occurring when solutions of mercury chloride and potassium iodide are mixed together.

$$\underset{\text{Mercury chloride.}}{HgCl_2} + \underset{\text{Potassium iodide.}}{2KI} = \underset{\text{Mercury iodide.}}{HgI_2} + \underset{\text{Potassium chloride.}}{2KCl.}$$

With the assistance of a table of atomic weights, the chemist learns from this equation that a molecule of mercury chloride, consisting of one atom of mercury, weighing 200, together with two atoms of chlorine, each weighing 35·37; and two molecules of potassium iodide, each consisting of one atom of potassium, weighing 39·1, and one atom of iodine, weighing 126·6, together yield or produce one molecule of mercury iodide, consisting of one atom of mercury, weighing 200, and two atoms of iodine, each weighing 126·6; and two molecules of potassium chloride, each of which contains one atom of potassium, weighing 39·1, and one atom of chlorine, weighing 35·37. **As no chemical change affects the weight of matter, the weight of the quantity of a compound represented by its formula must be the sum of those of the constituent elements; so, too, the weight of the bodies resulting from a chemical change must be the same as that of the bodies before the change, whatever it may be, had occurred.** Also the same number of atoms of each element must appear on each side of the equation. Although from a chemical equation and table of atomic weights it is possible to state what relative weight of each element is concerned in any chemical action, it must never be

forgotten that **the combining weights were first determined by experiment, and then the table compiled therefrom.**

CHAPTER II

OXYGEN AND OZONE

Oxygen.—Symbol, O. Atomic weight, 15·96. Density, 15·96. Specific gravity, 1·1056. Molecular formula and weight, O_2, 31·92. Boiling point, $-130°$ C. under 475 atmospheres.

The density of a gas is its weight, volume for volume, compared with hydrogen taken as unity; the specific gravity is its weight compared with that of an equal volume of air.

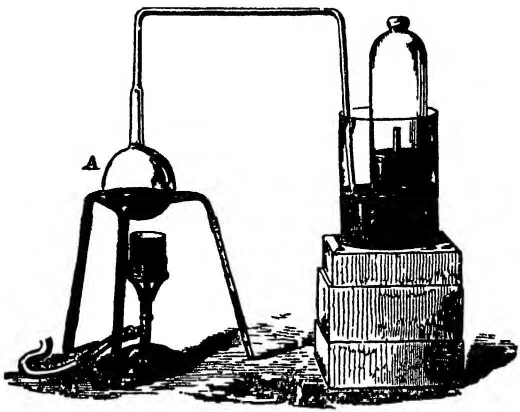
24. **Occurrence.**—Oxygen occurs plentifully in nature, both in the free state and in combination with other elements. About one-fifth of the atmosphere consists of this gas in the elementary form. Water contains eight-ninths of its weight of oxygen, and of the earth's crust some 48 per cent. consists of this element.

25. **Discovery.**—The credit for the discovery of this gas has been claimed by Lavoisier, and also by Priestley of Birmingham; to the latter, however, it undoubtedly belongs. Priestley discovered, in 1774, that on heating mercury in contact with air a remarkable change ensued. To study this chemical action the apparatus shown in fig. 4 may be employed.

The flask A is provided with a neck of considerable length, so bent as to pass up into the interior of the bell-jar shown in the figure. Into this retort one or two ounces of mercury are introduced; the vessel containing the bell-jar is also partly filled with mercury. The result is that direct communication exists between the air in the flask and that in the bell-jar; while both are cut off from the external atmosphere. The flask is next heated to very nearly, but not quite,

the boiling-point of mercury, and maintained at that temperature for some days. Gradually the enclosed volume of air becomes less, and on allowing the mercury to cool, red scales are seen to have been formed on its surface. These red scales

FIG. 4.



consist of mercury oxide, and have been formed by the combination of mercury with the free oxygen of the atmosphere according to the following equation—

$$\underset{\text{Mercury.}}{2Hg} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Mercury oxide.}}{2HgO.}$$

On removing these red scales and subjecting them to a stronger heat, they are again decomposed into mercury and oxygen—

$$2HgO = 2Hg + O_2.$$

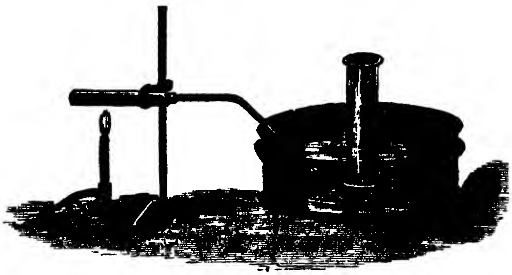
In this way oxygen gas was first discovered and isolated.

26. Preparation.—Oxygen can be obtained from the oxide of mercury as has been just described; but the oxide itself is much more conveniently prepared by other and less direct methods than those employed by Priestley.

A tube of difficultly fusible glass (combustion-tubing) is prepared, and to it a cork and delivery tube are attached. The tube is partly filled with mercury oxide, and arranged

as in fig. 5, with the delivery tube leading into a pneumatic trough. The mercury oxide is heated by means of a bunsen burner, and slowly decomposes ; the oxygen passes over into the jar arranged in the trough, and metallic mercury condenses

FIG. 5.



in the cooler parts of the combustion-tube. This method of preparing oxygen is only employed as an illustration of the historical process, as mercury oxide is expensive, gives off but a small proportion of its weight as oxygen, and that at only a comparatively high temperature.

It may be well here to explain the principle on which gases are collected over water or other liquid in the pneumatic trough. In fig. 5 the front of the trough is cut away so as to exhibit the beehive shelf on which the gas jar stands. This beehive is a vessel shaped somewhat like a gallipot, with a hole in its side and another through the bottom. The gas jar is first filled with water and then placed on the beehive shelf in an inverted position. The leading tube from the gas-generating apparatus is inserted through the side of the beehive shelf, and the gas in bubbling upwards displaces the water in the jar. As soon as the latter is full its mouth is covered with a ground-glass plate, the face of which has been greased. Another jar is placed in position and filled. This operation proceeds until sufficient gas is collected. Unless a gas is soluble in water this is the most convenient method of collecting it for general laboratory purposes. At times, gases are collected over mercury instead of water, while with very soluble gases the plan is adopted of collecting them by 'displacement.'

Oxygen is now most frequently prepared, for laboratory purposes, by heating a salt termed potassium chlorate, $KClO_3$, when the whole of the oxygen is evolved, and potassium chloride only remains. The reaction occurs in three distinct stages, according to the following equations. First the potassium chlorate is decomposed into potassium chlorite and perchlorate.

$$\underset{\text{Potassium chlorate.}}{2KClO_3} = \underset{\text{Potassium chlorite.}}{KClO_2} + \underset{\text{Potassium perchlorate.}}{KClO_4}.$$

Almost simultaneously the potassium chlorite is decomposed into potassium chloride and oxygen.

$$\underset{\text{Potassium chlorite.}}{KClO_2} = \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Oxygen.}}{O_2}.$$

At a much higher temperature, the potassium perchlorate is also decomposed into potassium chloride and oxygen.

$$\underset{\text{Potassium perchlorate.}}{KClO_4} = \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Oxygen.}}{2O_2}.$$

For ordinary purposes the whole of the equations may be grouped together, showing only the final, and not the intermediate results, thus—

$$\underset{\text{Potassium chlorate.}}{2KClO_3} = \underset{\text{Potassium chloride.}}{2KCl} + \underset{\text{Oxygen.}}{3O_2}.$$

Oxygen in a very pure form may be thus obtained, but the temperature at which it is evolved is somewhat high; admixture of about one-quarter the weight of manganese dioxide with the potassium chlorate causes the gas to be evolved at a much lower temperature and with much greater rapidity; the manganese dioxide itself is found unchanged at the end of the reaction; why this and some other substances act in this manner is not well understood. The gas obtained from the mixture is not quite so pure as that from the chlorate only, but is sufficiently so for most purposes.

Many other of the metallic oxides (compounds of metals with oxygen) evolve oxygen on being heated. Among these

is manganese oxide, which is decomposed at a red heat into a compound containing a higher proportion of the metal, and into free oxygen :—

$$\underset{\text{Manganese dioxide.}}{3MnO_2} = \underset{\text{Manganese tetroxide.}}{Mn_3O_4} + \underset{\text{Oxygen.}}{O_2}.$$

Prior to the employment of potassium chlorate, this was the usual method of preparing oxygen : a piece of iron tubing was closed at one end and partly filled with the manganese oxide ; to the other end a delivery tube was attached. The iron tube was placed in a fire or furnace, and oxygen gas was evolved.

Lead peroxide may be mentioned as another oxide which undergoes a somewhat similar decomposition under the influence of heat:—

$$\underset{\text{Lead peroxide.}}{2PbO_2} = \underset{\text{Lead monoxide.}}{2PbO} + \underset{\text{Oxygen.}}{O_2}.$$

There is another somewhat important class of chemical actions in which oxygen is liberated in the free state; a full explanation of these is not practicable at present, but it may be stated that certain metals can form compounds in which a high proportion of oxygen is present; when they are caused to enter into combination with other substances in which the proportion of oxygen is less, that element is set at liberty. The following is an example of such a reaction:—

$$\underset{\substack{\text{Potassium}\\\text{bichromate.}}}{K_2Cr_2O_7} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{4H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4} + \underset{\substack{\text{Chromium}\\\text{sulphate.}}}{Cr_2(SO_4)_3} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Oxygen.}}{3O}.$$

Reference will subsequently again be made to reactions of this type.

27. Manufacture.—As distinct from 'preparation,' under which head laboratory processes are explained, it is intended to describe under the heading 'manufacture' those methods employed for the production of substances on a large scale for commercial purposes.

Until recently the only practicable method of manufacturing oxygen was by heating the mixture of potassium chlorate and manganese dioxide, in large quantities, in suitable iron retorts

There is another reaction known by which oxygen may be obtained from the atmosphere, in which there is an inexhaustible supply, provided we can only economically effect its separation. Barium oxide, at a dull red heat, absorbs oxygen and forms barium peroxide; at a still higher temperature the absorbed oxygen is once more liberated, and this cycle of operations may be continued indefinitely. The changes are thus represented:

$$\underset{\text{Barium oxide.}}{2BaO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Barium peroxide.}}{2BaO_2}.$$

$$\underset{\text{Barium peroxide.}}{2BaO_2} = \underset{\text{Barium oxide.}}{2BaO} + \underset{\text{Oxygen.}}{O_2}.$$

It has been discovered comparatively recently that the same changes occur with a constant temperature, provided the pressure is varied. Brin's Oxygen Company now works this process for the manufacture of oxygen in the following manner. The barium oxide is heated to a suitable temperature in convenient receptacles, air being forced in under pressure. The oxygen is gradually absorbed, and when the stage of saturation is reached the pressure is removed and the absorbed gas recovered by exhaustion with vacuum-pumps. Alternately air is pumped in, the nitrogen allowed to escape, and oxygen then pumped out.

28. Properties.—Oxygen is a colourless, odourless, tasteless, neutral, and non-inflammable gas, which, until 1877, had never been liquefied, and hence was formerly termed a 'permanent' gas. Oxygen is slightly heavier than air, and 15·96 times the density of hydrogen. It is slightly soluble in water, one hundred volumes of water at 15° C. dissolving about three volumes of oxygen. With a rise in temperature the quantity absorbed is less, and, by boiling, water can be almost entirely freed of the dissolved oxygen. Oxygen is also dissolved by several of the metals when in a state of fusion. Silver is the best known example. As the metal solidifies, the oxygen is liberated, thus giving rise to what is called the 'spitting' of silver. Oxygen is distinguished from all other gases by its most important property of supporting respiration. Oxygen in

its pure state is far too active to perform this function satisfactorily; in the atmosphere this difficulty is overcome by the presence of nitrogen, which acts as a diluting agent, there being approximately four volumes of nitrogen to one of oxygen in the air. Although the quantity of oxygen capable of being dissolved by water is so small, yet that amount possesses a most important function in nature, the breathing of fishes being supported by this dissolved oxygen.

Oxygen also supports the combustion or burning of inflammable bodies; it is because of its presence in the air that such bodies burn under ordinary conditions. All such substances burn with increased brilliancy in the pure gas. Thus a splinter of glowing wood bursts into flame on being introduced into a jar of oxygen, a property which serves as a usual test for the gas. When comparing oxygen with some of the substances produced by combustion in it, it is well to remember that it has no action on lime-water, neither does it change the colour of a solution of litmus. (Litmus is a vegetable product of a blue colour.) Both these properties are capable of easy verification by experiment. A piece of charcoal heated to redness in a deflagrating spoon and then plunged into the gas burns most brightly; at the close of the combustion the residual gas is found to turn lime-water milky, a property characteristic of carbon dioxide gas:—

$$\underset{\text{Carbon.}}{C} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Carbon dioxide.}}{CO_2}.$$

Sulphur and phosphorus both burn with remarkable brilliancy in oxygen, the former producing sulphur dioxide gas, the latter phosphorus pentoxide, a very deliquescent [1] white solid:—

$$\underset{\text{Sulphur.}}{S} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Sulphur dioxide.}}{SO_2}.$$

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Oxygen.}}{5O_2} = \underset{\text{Phosphorus pentoxide.}}{2P_2O_5}.$$

Both sulphur dioxide and phosphorus pentoxide change the colour of the blue solution of litmus to a bright red. Suitable

[1] Bodies are termed deliquescent which absorb moisture from the air, becoming damp, and sometimes perfectly liquid, as a result.

precautions being taken, the metal sodium may be burned in oxygen, with the production of solid sodium oxide :—

$$\underset{\text{Sodium.}}{4Na} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Sodium oxide.}}{2Na_2O.}$$

Sodium oxide readily dissolves in water, and changes the colour of litmus solution reddened by the addition of phosphorus pentoxide, or other substances having a similar action, back once more to the original blue. Iron is one of the metals comparatively easily burned in oxygen. If a piece of fine iron wire be coiled into a helix, as shown in fig. 6, and then a piece of wax vesta be attached to the end, it may be caused to burn in oxygen gas. The gas should be contained in a jar open top and bottom ; the lower end is stood in a shallow vessel filled with water, having a sheet of paper below the surface. The vesta is lighted and the coil of wire immediately plunged into the gas, when it burns with most brilliant scintillations, forming molten drops of iron oxide, which, were it not for the intervention of the paper, would fuse themselves into the glaze of the dish at the bottom, notwithstanding the presence of the water.

FIG. 6.

$$\underset{\text{Iron.}}{3Fe} + \underset{\text{Oxygen.}}{2O_2} = \underset{\text{Iron tetroxide.}}{Fe_3O_4.}$$

If the iron oxide produced in this experiment be carefully collected and weighed, it is found to be heavier than was the iron before its combustion. This iron oxide is not soluble in water, and is without action on litmus solution.

29. Industrial Applications.—It is only comparatively recently that the industrial application of pure oxygen has been seriously considered. It is at present used in conjunction with hydrogen or coal-gas for the purpose of producing a very

brilliant light by the intense ignition of lime. Oxygen is also employed in the fusion of platinum, and with cheaper modes of commercial production may in the future be used in other metallurgical operations. During the past year it has been discovered that chlorine bleaching compounds have their energy much increased by the presence of oxygen in their solution.

30. Oxides.—This name is applied to the class of bodies produced by the combination of elements with oxygen. The whole of the elements, with the single exception of fluorine, form one or more oxides, the character of which varies with the nature of the combining element, and the number of atoms of each element in the compound. One of the most important distinctions between oxides is the property in virtue of which certain members of this group redden a solution of litmus, while others restore to such reddened litmus its blue colour; other oxides hold an intermediate position, producing no change in the colour of litmus and showing none of the other properties associated with these litmus colour-changes. The oxides which redden litmus, produce by combination with water a series of bodies termed *acids*, and are called acid-forming oxides or anhydrides, while those which restore the blue colour are known as *bases*, or basic oxides. The basic oxides are mostly compounds of the metals with a low proportion of oxygen; compounds of some of the metals with higher proportions of oxygen, and also the oxides of most of the non-metals, are acid-forming oxides. The 'intermediate' oxides are compounds of a few metals. There is yet a fourth class of metallic oxides characterised by the presence of very high proportions of oxygen, which do not form acids and which are readily decomposed by heat, with the evolution of oxygen in the free state; these are usually termed peroxides. Although many oxides are very distinctive in their character, there are others which it is difficult to class; they act as weak bases under certain conditions, and form weak acids under others. Examples of the various classes of oxides are given in the following table:—

Basic Oxides	Acid-forming Oxides	'Intermediate' Oxides	Peroxides
Sodium oxide, Na_2O	Sulphur dioxide, SO_2		
Potassium oxide, K_2O	Sulphur trioxide, SO_3		
Calcium oxide, CaO	Phosphorus pentoxide, P_2O_5		
Copper oxide, CuO	Carbon dioxide, CO_2		
Cuprous oxide, Cu_2O	Nitrogen pentoxide, N_2O_5		
Barium oxide, BaO			Barium peroxide, BaO_2
Manganese oxide, MnO	Manganic anhydride, MnO_3(?)	Manganese tetroxide, Mn_3O_4	Manganese dioxide, MnO_2
Manganese sesquioxide, Mn_2O_3	Permanganic anhydride, Mn_2O_7(?)		
Chromium oxide, CrO; Chromium sesquioxide, Cr_2O_3	Chromic anhydride, CrO_3	Chromium tetroxide, Cr_3O_4	Chromium dioxide, Cr_2O_4
Iron oxide, FeO; Iron sesquioxide, Fe_2O_3	Ferric anhydride, FeO_3(?)	Iron tetroxide, Fe_3O_4	
Lead oxide, PbO		Lead tetroxide, Pb_3O_4	Lead dioxide, PbO_2

Those oxides to which a note of interrogation (?) is attached have not as yet been isolated in the free state, although their corresponding acids or other compounds are known. The intermediate oxides are usually viewed as compounds of other oxides with each other; thus iron tetroxide may be considered as a compound of the monoxide FeO with the trioxide Fe_2O_3, and may have its formula written FeO,Fe_2O_3.

31. **Tests for Oxygen.**—Oxygen is commonly recognised by its property of rekindling into a flame a glowing splinter of wood; this property it possesses in common with nitrous oxide, N_2O. The addition of nitrogen dioxide, NO, to any gas containing free oxygen immediately causes the development of a reddish-brown tint, owing to the formation of nitrogen peroxide, NO_2. As nitrous oxide does not produce this reaction, the two gases are thus readily distinguished. If a mixture be made of solutions of potassium hydrate, KHO, and pyrogallic acid, this liquid rapidly absorbs oxygen and acquires a dark-brown colour. By the aid of this reagent oxygen is removed from other constituents of a gaseous mixture.

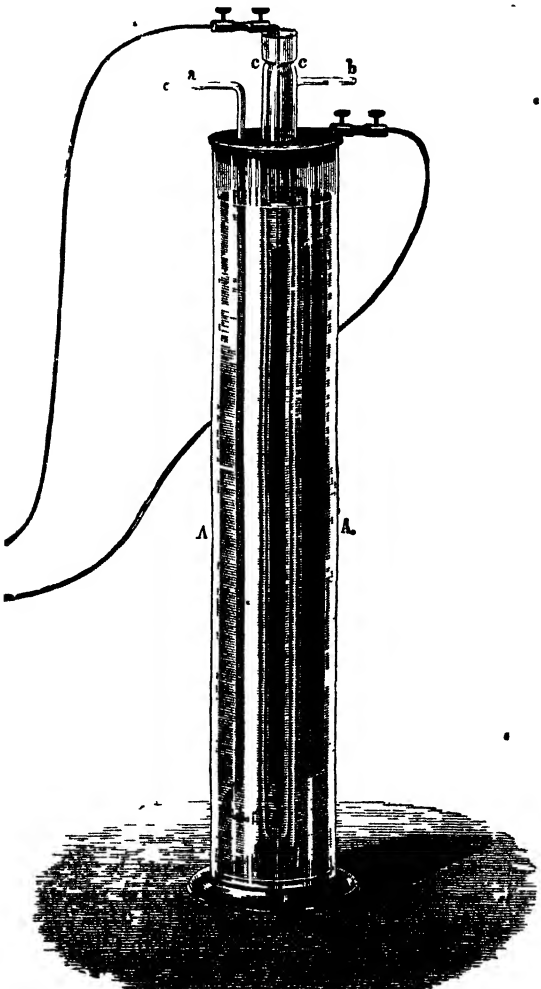
Ozone (Allotropic Oxygen). — Density, 23·94. Specific gravity, 1·6584. Molecular formula and weight, O_3, 47·88.

32. **Occurrence.**—Ozone is an interesting modification of oxygen, of which traces are found in the air near the seaside and in the open country. It is produced when a frictional electric machine is being worked, and especially during the operation of the modern Voss and other similar type induction machines. Its presence is then easily recognised by its peculiar odour, which has given rise to the term 'electric smell' applied to the ozone thus formed.

33. **Preparation.**—Ozone is best prepared by the action of an electric discharge on oxygen, and it is in this manner that the electric machines produce ozone. The passage of an electric spark destroys much of the ozone almost simultaneously with its formation, hence some contrivance is necessary in which a *silent* discharge occurs, that is a discharge unaccompanied by sparks. For this purpose, the discharge should occur between two surfaces of large area, a slow current of oxygen being passed between the two surfaces. The apparatus shown in fig. 7 is arranged on this principle, and consists of an outer glass cylinder, A A, to which is attached a wooden cover. Through the centre of this lid passes a wide glass tube, open at the top and closed at the bottom. Near to its lower end a piece of quill glass tubing is sealed and bent over so as to pass through the cover; this end is marked *a*. These tubes together form a U-tube, having one wide and one narrow limb. Inside the wider tube, another of smaller size is introduced, also leading almost to the bottom, but quite closed, like a test-tube. At the line C C this inner tube is fixed to the outer one so as to make an airtight joint; at *b* a piece of quill tubing is 'blown' into the wider tube. Gas may be passed in through *b*, and after traversing the narrow annular space between the two tubes, it emerges at the bottom and passes upwards through the piece of quill tubing, emerging at *a*. To use the apparatus, the inner tube and outer cylinder are both filled to nearly the top with dilute sulphuric acid (1 to 10), and a platinum elec-

trode caused to dip in each. (These electrodes consist of pieces of platinum foil threaded on to stout wires of the same

FIG. 7.



metal.) The electrodes are attached by means of binding-screws to the wires leading from a powerful induction coil, the electric current from which is conducted by the dilute acid to the surfaces of the tubes arranged within each other, and then passes across the ring-like space between as a silent discharge. On passing a slow current of dry oxygen in through *b*, the emergent gas at *a* is found to possess the characteristic odour of ozone. Under the most favourable circumstances, however, the quantity of ozone produced by the transformation of oxygen does not amount to more than about one-sixth of the out-flowing gas.

Ozone is also formed during the slow oxidation of phosphorus and other substances in air, among them being oil of turpentine and other essential oils. The oxygen evolved by the decomposition of potassium bichromate and potassium permanganate usually contains small quantities of ozone. So also does that evolved during the decomposition of water by means of an electric current (electrolysis).

34. **Properties.**—Ozone is a gas having a density just 1·5 times that of oxygen. It has a faint, peculiar odour, sometimes described as resembling that of chlorine. Ozone is distinguished by its powerful oxidising properties. Many of the metals, including even those so difficultly oxidisable as copper, mercury, and silver, are rapidly converted by ozone into oxides. During oxidation by ozone no diminution in the volume of the gas occurs. The extra density shows that in ozone three volumes of oxygen occupy the space of two volumes of the ordinary gas; hence the view that the ozone molecule contains three atoms instead of two as in oxygen. Oxidation by ozone may be represented by the equation:—

$$\underset{\text{Ozone.}}{O_3} + \underset{\text{Silver.}}{2Ag} = \underset{\text{Silver oxide.}}{Ag_2O} + \underset{\text{Oxygen.}}{O_2}.$$

The oxidising power of ozone leads it to immediately decompose potassium iodide when the two are brought into contact, oxidising the potassium and liberating free iodine:—

$$\underset{\text{Ozone.}}{O_3} + \underset{\text{Potassium iodide.}}{2KI} + \underset{\text{Water.}}{H_2O} = \underset{\text{Potassium hydrate.}}{2KHO} + \underset{\text{Iodine.}}{I_2} + \underset{\text{Oxygen}}{O_2}.$$

One characteristic of free iodine is that it forms a deep blue-coloured compound on coming in contact with starch. These properties of ozone and iodine respectively enable us to test for ozone. Papers are prepared by being dipped in a solution of potassium iodide and starch. Such papers are colourless, but on exposure to ozone, iodine is liberated, and that element develops a blue colour in the starch. In common with ozone the higher oxides of nitrogen and certain other bodies possess this property, so that the test is not an absolutely decisive one for ozone. Ozone slowly decomposes into oxygen at ordinary temperatures; the same change takes place instantaneously at a temperature of about 237° C.; at the same time the gas regains its original volume. The presence of ozone in the atmosphere is demonstrated by the fact that at times air which produces a blue colour with iodide of starch papers, ceases to do so after having been heated to 237° C.: any colouring power due to the presence of oxides of nitrogen would not thus be destroyed. Air contaminated with organic matter is rapidly de-ozonised, owing to the reducing action of such bodies, consequently ozone is rarely found in the air of cities or large towns.

Ozone is soluble in water, and imparts to it its characteristic odour. The colour of a solution of indigo is destroyed by the action of ozone, colourless compounds being formed which contain a higher proportion of oxygen. It is possible that with the development of cheap oxygen-manufacturing processes, ozone may in the future be somewhat largely used as a bleaching agent.

35. **Composition.**—Oil of turpentine possesses the power of absorbing ozone entirely without decomposition; if two portions of ozonised oxygen be taken from the same vessel, and the one portion be submitted to the action of oil of turpentine, a diminution of volume occurs. If the other portion be heated to 237° C. an increase of volume follows; the amount of increase in volume is just double that of the contraction when oil of turpentine is used as an absorbent. Supposing that 30 volumes of the ozonised oxygen diminished

to 27 on treatment with oil of turpentine, then there were three volumes of ozone present. As another 30 volumes of the same gas expands to 31·5 volumes on being passed through a tube heated to over 237° C., then we know that three volumes of ozone have yielded 4·5 volumes of oxygen. In this way we learn that three volumes of oxygen condense to form two volumes of ozone, and that on being re-converted into oxygen the gas expands to its original volume. Andrews has demonstrated very clearly how oxidation is caused by this gas. Oxygen was first transformed into ozone to as great an extent as possible by means of an apparatus somewhat similar to that previously described, but so arranged that any diminution in the volume of the gas is exactly measured. Prior to the commencement of the experiment a hermetically sealed glass bulb containing potassium iodide was introduced into the apparatus; this, after its conclusion, was broken, and the iodide decomposed by the ozone; this chemical action was unaccompanied by any diminution in volume, showing that the liberated oxygen occupied the same space as did the ozone, and that ozone-oxidation is caused by the extra atom of oxygen in the molecule.

36. **Allotropy.**—Although oxygen and ozone present striking differences from each other, yet they are simply modifications of one and the same element. It has been shown that there is in this case a very simple difference in the constitution of the molecules, one containing two, and the other three atoms. Other elements also exist in two or more forms, due probably either to variations in the number of atoms in the molecule, or to variations in the method of their arrangement to form the molecule. **When an element occurs in two or more distinct forms it is said to exhibit allotropy, and the less common varieties are said to be allotropic forms of that element.** For this reason ozone is sometimes termed 'allotropic oxygen.'

CHAPTER III

HYDROGEN

Symbol, H. Atomic weight, 1. Density, 1. Specific gravity, 0·0691. Molecular formula and weight, H_2, 2. Boiling-point, −140° C. under 650 atmospheres.

37. **Occurrence.**—Hydrogen occurs in the free state in the gases evolved from certain volcanoes, and at times among the products of putrefaction. Spectrum analysis also reveals free hydrogen as a constituent of certain stars and nebulæ. Hydrogen is chiefly found in combination with oxygen in water, which compound consists of one part of hydrogen united with eight parts of oxygen by weight. Most, if not all, organic substances (*i.e.* compounds of either animal or vegetable origin) contain hydrogen. This gas was discovered by Paracelsus in the sixteenth century, and was systematically investigated by Cavendish, who, in 1781, demonstrated the elementary nature of this gas.

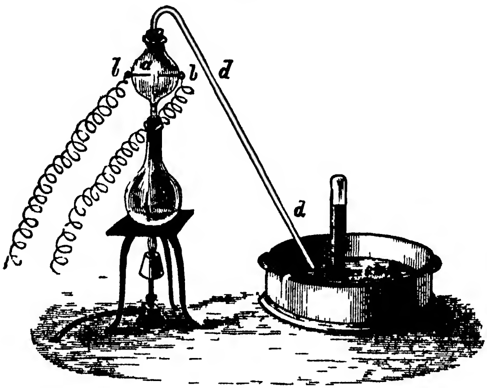
38. **Preparation.**—Theoretically the simplest method of preparing hydrogen is by the decomposition of water into its constituent elements:—

$$\underset{\text{Water.}}{2H_2O} = \underset{\text{Hydrogen.}}{2H_2} + \underset{\text{Oxygen.}}{O_2}.$$

The decomposition of water may be effected by intense heat, but the difficulty is that as the gases cool down, they once more combine and water is again produced. The most convenient source of heat for the purpose is that of the electric spark. The apparatus used consists of a glass bulb, *a*, through which platinum wires, *b b*, are fixed, so that their ends are in the centre of the bulb and about an eighth of an inch apart. This apparatus is attached by means of a glass tube to a flask, *c*, containing boiling water, the steam evolved from which passes through the bulb, and by means of a leading tube, *d d*,

is conveyed over into the pneumatic trough, in which is arranged a gas jar and beehive shelf. The steam from the boiling water is allowed to pass until all air is expelled, the steam itself being condensed by the cold water in the trough.

FIG. 8.



At this stage a series of sparks from an induction coil is passed through the wires *b b*. The passage of each spark decomposes a small quantity of steam, and the mixed gases being immediately largely diluted with steam, some proportion at least is kept apart until the gases have cooled below their combining temperature. In this way the gas jar is slowly filled with an explosive mixture of hydrogen and oxygen, which would have to be separated before hydrogen could be obtained in the pure state.

The most convenient method of effecting the direct decomposition of water is by electricity (electrolysis), an operation which is described in detail in the next chapter.

Ordinarily hydrogen is obtained from water by the action of certain metals, which have a great attraction for oxygen. Solid metallic compounds with oxygen are thus formed, and the hydrogen escapes in the free state. One of the most active metals of this kind is potassium. If a small piece of this metal is thrown on water, violent chemical action immediately ensues,

and hydrogen gas is evolved, which, however, immediately takes fire, owing to the high temperature caused by the chemical combination of the potassium with the oxygen of the water. Sodium produces a similar but less violent reaction, and usually the gas is evolved without burning; on being thrown on the water the metal melts and moves about rapidly, causing a slight hissing noise, and gradually disappearing. If the fragment of sodium be enclosed in some fine wire gauze, and thus held underneath the surface of the water, bubbles of hydrogen rise to the surface, and may be collected in a gas jar in the ordinary manner. Under these circumstances the following reactions occur :—

$$\underset{\text{Potassium.}}{2K} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Potassium hydrate.}}{2KHO} + \underset{\text{Hydrogen.}}{H_2}.$$

$$\underset{\text{Sodium.}}{2Na} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sodium hydrate.}}{2NaHO} + \underset{\text{Hydrogen.}}{H_2}.$$

In these reactions it should be observed that one atom only of the two atoms of hydrogen present in water is replaced by the metal. If the solution of sodium hydrate be evaporated to dryness, and then carefully heated with more sodium, it is possible to get the second atom of hydrogen displaced thus :—

$$\underset{\text{Sodium hydrate.}}{2NaHO} + \underset{\text{Sodium.}}{2Na} = \underset{\text{Sodium oxide.}}{2Na_2O} + \underset{\text{Hydrogen.}}{H_2}.$$

Making use of an atomic instead of a molecular equation, the two successive displacements of hydrogen may be thus represented :—

$$\underset{\text{Water.}}{HHO} + \underset{\text{Sodium.}}{Na} = \underset{\text{Sodium hydrate.}}{NaHO} + \underset{\text{Hydrogen}}{H}.$$

$$\underset{\text{Sodium hydrate.}}{NaHO} + \underset{\text{Sodium.}}{Na} = \underset{\text{Sodium oxide.}}{NaNaO} + \underset{\text{Hydrogen.}}{H}.$$

$$\underset{\text{Sodium oxide.}}{NaNaO}.$$

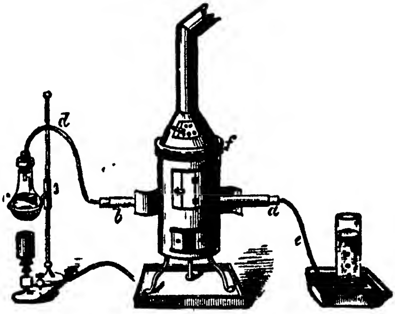
Written in this manner, the replacement of the hydrogen by sodium in two steps is shown very clearly. Instead of using sodium for the replacement of this second atom of

hydrogen, zinc or aluminium may be substituted; these metals have the advantage of being more easily manipulated than is sodium. With zinc the reaction becomes :—

$$\underset{\text{Sodium hydrate.}}{2NaHO} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Sodium zinc oxide.}}{ZnNa_2O_2} + \underset{\text{Hydrogen.}}{H_2}.$$

A number of other metals beside sodium and potassium also decompose water, some at ordinary and others at higher temperatures. Among the latter is iron, which at a red heat decomposes water with great readiness. A convenient form of apparatus is that shown in fig. 9, which consists of an iron tube, *a b*, filled with coarse iron turnings, and passed through a furnace *f*, so that the ends may project. To the end of the tube *b* is attached the leading tube from a flask containing boiling water, *c*; the other end, *a*, of the iron tube is connected with the gas jar, *j*, arranged in the pneumatic trough. The iron tube and its contents of iron fragments are heated to redness by the furnace, and then a current of steam passed through; hydrogen escapes in large quantities, and an iron oxide is formed :—

FIG. 9.

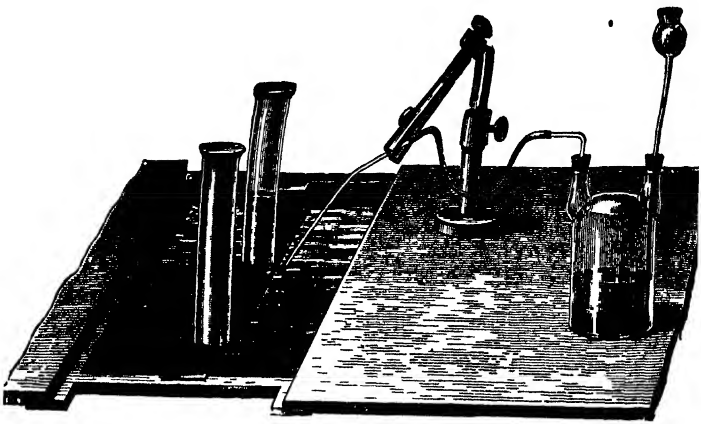


$$\underset{\text{Iron.}}{8Fe} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Iron tetroxide.}}{F_3O_4} + \underset{\text{Hydrogen.}}{4H_2}.$$

The most convenient method of preparing hydrogen for laboratory purposes is by the action of either iron or zinc on dilute hydrochloric or sulphuric acids. The hydrogen of these bodies is readily displaced by either of the metals mentioned at ordinary temperatures. Usually zinc and sulphuric acid are employed. The zinc is either granulated or cut into clippings; these are inserted in a glass flask, or double-necked (Woulff's) bottle, fitted with thistle-funnel and delivery-tube The acid

is diluted with from four to six times its volume of water, and added through the thistle funnel. The evolution of hydrogen gas immediately commences, and the acid in the flask rises rapidly in temperature. The gas is collected over the pneumatic trough, as shown in fig. 10.

FIG. 10.



The following equations show the reactions which occur with zinc and iron respectively :—

Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2.
Zinc.		Sulphuric acid.		Zinc sulphate.		Hydrogen.
Zn	+	$2HCl$	=	$ZnCl_2$	+	H_2.
Zinc.		Hydrochloric acid.		Zinc chloride.		Hydrogen.
Fe	+	H_2SO_4	=	$FeSO_4$	+	H_2.
Iron.		Sulphuric acid.		Iron sulphate.		Hydrogen.
Fe	+	$2HCl$	=	$FeCl_2$	+	H_2.
Iron.		Hydrochloric acid.		Iron chloride.		Hydrogen.

In preparing hydrogen great care must be taken that the gas is free from oxygen or air before a light is applied, as otherwise an explosion will ensue. The gas should be allowed to escape for a time, and then a small jar collected and tested

by applying a lighted taper to the mouth. The gas should burn quietly without explosion.

Although commercial zinc is so well adapted for the preparation of hydrogen from sulphuric acid, yet perfectly pure zinc is without action on the dilute acid. Commercial zinc contains traces of other metals, and these, being in contact with the zinc, set up a voltaic (electric) action, by means of which the acid is decomposed and hydrogen evolved. This effect of the impurities of ordinary zinc may be avoided by coating the zinc with mercury. The zinc is first thoroughly cleansed with sulphuric acid, and then rubbed over with mercury until the whole surface is amalgamated (i.e. covered with an alloy of mercury with zinc). Zinc so treated gives off no hydrogen on being immersed in dilute sulphuric acid. The addition of a few drops of copper sulphate to the acid and pure zinc causes a deposit of metallic copper on the zinc, and as a result hydrogen gas is at once evolved. The copper sulphate is, under these circumstances, decomposed, with the simultaneous formation of zinc sulphate.

$$\underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Copper.}}{Cu.}$$

39. **Manufacture.**—As hydrogen is comparatively little employed on the large scale, it is scarcely an object of manufacture. The reaction most suitable for manufacturing purposes is that in which steam is passed over red-hot iron. The materials are of great cheapness, and the chemical change is of a simple character.

40. **Properties.**—Hydrogen is a colourless, odourless, tasteless, and inflammable gas, which does not support combustion. Hydrogen burns, when pure, with a pale blue flame, giving out very little light, but a great amount of heat. A mixture of hydrogen with either air or oxygen is violently explosive; consequently in preparing hydrogen it is essential that it be freed from these bodies before being brought in contact with a flame. Whenever hydrogen, or compounds containing hydrogen, burn or explode in air or oxygen, water

is formed from the hydrogen, according to the following equation :—

$$\underset{\text{Hydrogen.}}{2H_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Water.}}{2H_2O.}$$

Hydrogen is of very low density, being the lightest substance known ; it consequently diffuses itself with great rapidity through other gases. When subjected to great cold and pressure, hydrogen is condensed to a colourless liquid, which boils at about $-210°$ C., when under a pressure of 190 atmospheres.

Hydrogen gas is not poisonous, and may be breathed for a few seconds without injury, but animals placed in it speedily die, from simple deprivation of oxygen. It is very slightly soluble in water, 100 volumes of which only dissolve 1·93 volumes of the gas at all temperatures from 0° to 20° C.

Hydrogen possesses the peculiar property of readily permeating and diffusing through some of the metals when at a red heat. Among these the most noticeable are iron, platinum, and palladium. If hydrogen be passed through a red-hot palladium tube, the rate of escape through the walls of the tube is 0·399 cubic centimètres of gas for each square centimètre of surface exposed. The amount of hydrogen absorbed by palladium when red-hot, and still retained by it when cold, is 935 times the volume of the metal. On subsequently heating the palladium *in vacuo*, the hydrogen is again evolved. It is probable that under these circumstances a definite compound of palladium and hydrogen, PdH_2, is formed, which has the character of a solid alloy. In this alloy the hydrogen exists in the solid state, and has a calculated specific gravity of 0·62.

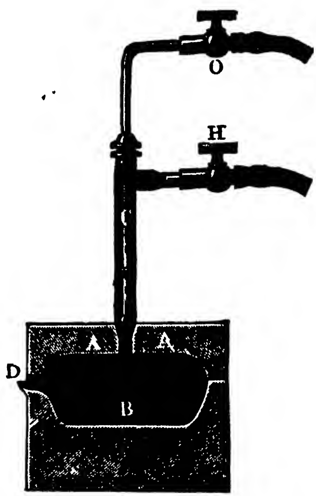
41. Industrial Applications.—The great buoyancy of hydrogen causes it to be of service for filling balloons. Ordinarily coal-gas is employed for this purpose, owing to its greater cheapness ; but for military purposes hydrogen is often preferred, as it may be manufactured by the red-hot iron and steam process, with much less cumbersome plant than is necessary for the preparation of coal-gas. When compressed

under very high pressure in iron cylinders, hydrogen is obtained in a fairly portable form.

The intense heat produced by the burning of hydrogen together with oxygen is of considerable service for the performance of certain metallurgical operations which require a very high temperature. Among these is the fusion of platinum, which is now effected in a furnace constructed of quicklime, and arranged as shown in fig. 11.

The lower block of quicklime has a cavity cut in it, marked B, for the reception of the metal. The lid, A A, constructed of the same material, has a hole bored through the centre, through which the nozzle of an oxy-hydrogen blowpipe is inserted. Close inspection shows that the tube marked C contains within it an inner tube or jet; the hydrogen enters through the screw-tap marked H, and passes down the space between the tubes, and is lit at the mouth of C. Through the screw-tap marked O, oxygen is admitted, and passing down through the jet meets the burning hydrogen at the end of the tube. To get the maximum temperature, the volumes of hydrogen and oxygen used must be in the proportion of two to one. This arrangement is termed an oxy-hydrogen blowpipe, and is first lighted and then inserted in its place in the cover, A A, of the furnace. The oxy-hydrogen flame impinges on the platinum in B, and speedily raises it to the melting-point, when it is run out into ingots through the spout D. The heat of the oxy-hydrogen blowpipe is put to another use in the lime-light. The flame of hydrogen burning in oxygen is only very faintly luminous, but its intense heat raises a cylinder of lime

FIG. 11.



to such a high temperature, that it emits a most brilliant and intense light, used for magic-lanterns and for signalling and other purposes.

42. Reducing and Oxidising Agents.—The ores or natural compounds from which metals are derived are in many cases oxides or sulphides of such metals. The operation of obtaining the metal in its free state is termed *reducing* the ore to the metallic state. Hence we get the definition that **a reducing agent is a substance which removes oxygen, or elements similar to it, from compounds.** Owing to the avidity with which hydrogen combines with oxygen, it constitutes one of the most powerful reducing agents with which we are acquainted. Thus, if hydrogen be passed over red-hot copper oxide, or iron oxide, the metal is obtained in the free state, according to the following equations :—

$$\underset{\text{Copper oxide.}}{CuO} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Copper.}}{Cu} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\text{Iron oxide.}}{Fe_2O_3} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\text{Iron.}}{2Fe} + \underset{\text{Water.}}{3H_2O.}$$

The former of these two reactions is of very considerable importance, as in the analysis of many compounds containing hydrogen, the hydrogen is thus converted into water and weighed as such. In addition to these instances, in which a reducing agent is employed in order to obtain metals in their free state, there are other examples of reduction in which the bodies are simply reduced to a lower stage of oxidation. Further, the same reducing agents are capable of removing, in whole or in part, chlorine and other similar elements from compounds. Among the most active reducing agents in addition to hydrogen, are carbon, carbon monoxide, zinc, sodium carbonate, and sulphurous acid.

We come next to a class of bodies which are just the exact opposite of the reducing agents; these are termed oxidising agents, and are described in the following definition :—**An oxidising agent is a substance which causes an element or compound to combine with oxygen or other elements of similar character.** Oxygen, and especially ozone are the

most familiar and direct examples of oxidising agents. If metallic copper be heated in a current of oxygen the following reaction occurs :—

$$\underset{\text{Copper.}}{2Cu} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Copper oxide.}}{2CuO.}$$

The following are some of the most important oxidising agents—oxygen, ozone, chlorine, bromine, potassium chlorate, nitric acid, and hydrogen peroxide.

43. **Nascent Condition of Elements.**—It has already been explained that the atoms of elements unite to form what are termed elementary molecules. It will be readily understood that some portion of the energy which impels atoms to unite with other atoms is thus consumed ; in consequence it is found that elements in the atomic state are more active than those same elements when in the molecular condition. To give an illustration : if a current of hydrogen be passed through a solution of ferric chloride, no change ensues, but if a few drops of sulphuric acid be added to the solution and then a fragment of zinc dropped in, bubbles of hydrogen are evolved, and almost immediately the colour is changed from a reddish colour to a very faint green tint, ferrous chloride being formed. In this second case the hydrogen is generated within the solution, and the liberated atoms at once act on the ferric chloride. In the first case the hydrogen has formed molecules, and has not sufficient energy to effect the reduction of the chloride. The following equations show the chemical changes which occur :—

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Nascent hydrogen}}{2H.}$$

$$\underset{\text{Nascent hydrogen.}}{2H} + \underset{\text{Ferric chloride.}}{Fe_2Cl_6} = \underset{\text{Ferrous chloride.}}{2FeCl_2} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

An essential of this type of chemical action is that it is caused by an element at the moment of its being liberated from a chemical compound. Therefore, **at the moment of liberation from a compound an element is said to be nascent, a word signifying being born.** Many elements

possess more active chemical properties when in the nascent state, the reasons for which should now be clear to the student. When elements are in the molecular state, the force by which the atoms are held together must be overcome before they can enter into fresh combinations. When they are in the nascent condition no such force has to be overcome, and so the atoms are able to enter into combinations much more readily.

CHAPTER IV

OXIDES OF HYDROGEN

Two oxides of hydrogen are known:—

Hydrogen monoxide, or water, H_2O.
Hydrogen peroxide, or hydroxyl, H_2O_2.

Water.—Formula, H_2O. Molecular weight, 17·96. Density, 8·98. Specific gravity as steam, 0·622. Specific gravity as liquid, 1·00. Melting-point, 0° C. Boiling-point, 100° C.

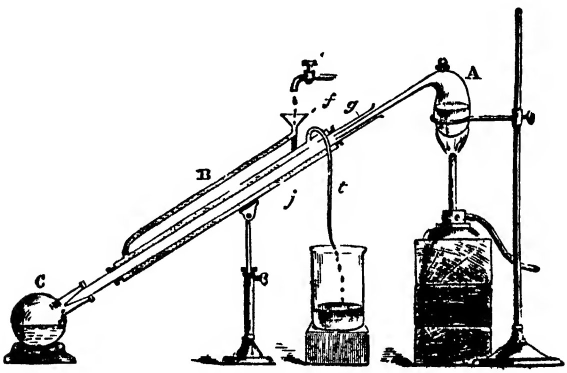
Water is taken as the standard of specific gravity of liquids and solids.

44. **Occurrence.**—Water is found in nature in the three distinct forms of ice, water, and steam. Its appearance and ordinary physical characters are so well known that any description is unnecessary.

45. **Preparation.**—Water naturally occurs so plentifully in an almost pure condition, that, except when required for chemical purposes, no special processes of preparation are needed. Chemically pure water is usually obtained by freeing natural water from the small quantity of foreign substances which it contains. As most of these are solid bodies in a state of solution, the water is commonly purified by the process of distillation. For small quantities the apparatus shown in fig. 12 may be employed.

On the right-hand side of the figure is shown a glass retort A, the stem of which is attached to the Liebig's condenser, B. This condenser consists of a glass tube *g*, surrounded with a jacket *j*, through which a current of cold water is passed from *f*. The lower end of the condenser-tube is placed within a receiving flask, marked C. In use, ordinary water is placed in the retort and boiled, the steam passes over into the condenser, and is there condensed by the cold water passing through the jacket. The water thus formed is gradually collected in the receiving flask and (when proper care is taken) is free from any solid matter, which remains behind in the retort. On the

FIG. 12.



large scale, a metal boiler is employed instead of the retort, and the condenser consists of a pure tin worm coiled within a tub, which is fed with a sufficient quantity of condensing water. This apparatus is termed a 'still,' and water thus purified is known as distilled water. The only impurities present in carefully prepared distilled water, are such volatile substances as distil over simultaneously with the water, and are re-dissolved in it as condensation occurs. In this way minute traces of ammonia are found in distilled water. When required in a condition of absolute purity, special methods are employed in order to expel these volatile impurities.

Water is formed as a secondary product in numberless

chemical reactions, but these can scarcely be considered as processes for its preparation. Thus water is always produced when a reaction occurs between an acid and a base, as for example:—

H_2SO_4	+	CaO	=	$CaSO_4$	+	H_2O.
Sulphuric acid.		Calcium oxide (base).		Calcium sulphate.		Water.

As a rule, whenever in a chemical action hydrogen and oxygen are liberated from other compounds, in each other's presence, they unite to form water, leaving only an excess of either, if present, in the free state.

46. **Properties.**—Between the temperatures of 0° and 100° C. water is a tasteless liquid, and without colour, except when seen in large masses. A layer of pure water some twelve feet in length, shows a faint greenish-blue tint. The most important property of water is its great solvent power, there being comparatively few substances which it does not dissolve in more or less quantity. In consequence, water is never found in a state of absolute purity in nature. The sea is the natural reservoir from which our water supplies are drawn. By the sun's heat, enormous quantities of sea-water are converted into vapour, which remains in the air in the gaseous form, or combines to produce clouds. Special atmospheric conditions lead to the precipitation of this moisture as snow or rain. This form of water is about the purest of those occurring naturally; but even rain-water is contaminated with gaseous impurities absorbed from the atmosphere, and also small quantities of solid matter which have been floating in the air in a minute state of subdivision. Rain and snow are the direct or indirect sources of spring and river waters; these always contain more or less solid matter, depending on the nature of the rocks and soil of each particular district. The rivers carry down with them solid matter to the ocean, which solid matter remains when the water is again evaporated to form clouds. There is thus a continuous, though slow, increase in the quantity of matter found in sea-water, which, as a result, has its well-known saline flavour. The constitution of sea-water varies in different parts; the following table shows its average composition:—

Water		96·470
Sodium chloride (common salt) NaCl . .	2·700	
Potassium chloride, KCl, ...	0·020	
Magnesium chloride, $MgCl_2$	0·360	
Calcium sulphate, $CaSO_4$	0·140	
Magnesium sulphate, $MgSO_4$	0·240	
Potassium sulphate, K_2SO_4	0·005	3·530
Calcium and magnesium carbonates, $CaCO_3$ and $MgCO_3$	0·004	
Bromine and iodine compounds, together with organic substances	0·011	
Carbon dioxide and volatisable organic substances	0·050	

From this table it will be seen that sea-water contains about 3½ per cent. of solid matters.

The composition of river water varies very considerably; thus the Dee, near Aberdeen, contains 5·72 parts per 100,000 of solid matter; while the Thames, at Battersea, yields 30·33 parts per 100,000. The one river flows through granitic and other hard and insoluble rocks; the other over the much softer and more soluble strata of the southern English counties.

In addition to the solid matters dissolved by water, the gaseous matters also present are of considerable importance. Ordinary drinking waters of good quality contain, on the average, about 0·8 per cent. of oxygen, 1·7 per cent. of nitrogen, and considerable quantities of carbon dioxide gas. The oxygen thus dissolved in water is the source of respiration of fishes, which are speedily suffocated in de-oxygenated water. The carbon dioxide renders the water much more palatable to the taste.

47. **Effects of heat on water.**—Among the properties of water, the physical changes it undergoes as a result of the application of heat are of such importance as to warrant a somewhat extended description. As is well known, at a temperature below the freezing-point water exists in the solid state and is known as ice. Taking a piece of ice at a temperature much below that at which it was formed, say $-20°$ C., the following is a history of its changes as a result of the continuous application of heat. As heat is first applied, the

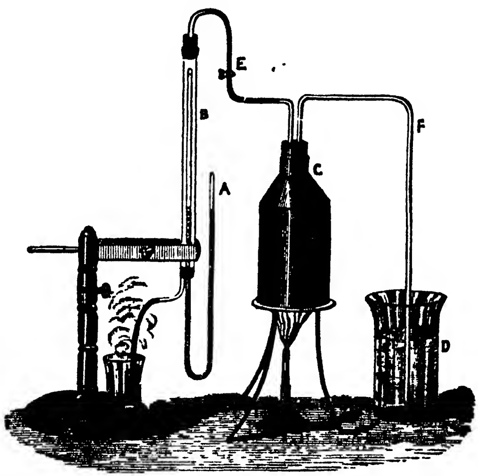
ice rises in temperature and at the same time increases in volume (expands); these changes proceed regularly until a temperature of 0° C. is attained. At that point the temperature remains stationary, notwithstanding that the absorption of heat continues. During this time the ice melts, and the heat thus absorbed without causing any corresponding elevation of temperature is employed in doing the work of converting the solid ice into liquid water. The heat necessary to melt a given weight of ice at 0° C. into water at the same temperature would raise the same weight of water from 0° to 79° C.; a fact which is expressed in other words by saying that the latent heat of water is 79 heat-units. During the melting of ice a considerable diminution in volume occurs, 10 volumes only of water being produced from 10·9 volumes of ice. As soon as the whole of the ice is melted, the temperature once more commences to rise, and does so steadily until a temperature of 100° C. is attained. The water at 0° C. diminishes in volume with an increase in temperature, until at 4° C., when it commences to expand, and continues to do so until 100° C. is reached. At 4° C., therefore, water is at its maximum density; either an increase or diminution of temperature results in expansion. At 100° C. the water commences to boil and remains stationary in temperature, but is not all at once converted into vapour; on the contrary, between five and six times as long is necessary to boil away the whole of the water as was requisite in order to raise it from the freezing to the boiling point. In exact figures, the quantity of heat necessary to convert a given weight of water into steam is sufficient to raise 537·2 times the weight of water from 0° to 1° C. The steam produced is at the same temperature, 100° C., as the boiling water; this large amount of heat is employed in the conversion of the water from the liquid to the gaseous state. The whole of the water having been converted into steam, a further application of heat results in the expansion of the steam, which follows the general laws governing the relation of gases to heat.

In cooling, steam passes through a series of changes which are just the converse to those it experiences on being heated. During the condensation of steam into water, and the solidifica-

tion of water to form ice, heat is liberated in the same quantity as was required in the first place to effect respectively the liquefaction of ice and the conversion of water into steam.

48. **Tension of Aqueous Vapour.**—At all temperatures, vapour is given off by water, with, as a result, the more or less rapid disappearance of the water by evaporation. The vapour thus evolved exerts a definite pressure, and this pressure increases as the temperature to which the water is subject rises. The pressure or tension of aqueous vapour may con-

FIG. 13.



veniently be studied in an apparatus such as is shown in fig. 13. The tube marked A is a U-tube, and should have the larger limb thirty-six inches long and sealed at the end, the shorter one being about half that length and open. This tube is enclosed within another, B, which serves as a steam or water jacket. For the earlier part of the experiment, the other part of the apparatus is not required. The longer limb of the U-tube A is to be filled with mercury, as is also the bend at the bottom. Proper precautions must be taken to ensure that

the tube and mercury are perfectly dry. On now placing the tube upright, it acts as a barometer; the vertical height from the surface of the mercury in the closed limb to that in the open one will be about thirty-one inches, but of course it varies with the barometric reading at the time. Let this be carefully measured, and one or two drops of water passed up into the vacuous space in the upper limb. This can be effected by filling the end, A, with water, and then inclining the tube so that a very small quantity passes up through the bend. On once more placing the tube in a vertical position and measuring the height of the mercury, a sensible depression will be noticed, even at ordinary temperatures. This depression must be caused by the pressure of the aqueous vapour, because beyond that there is nothing in the barometric vacuum of the instrument by which pressure can be exerted. The india-rubber tube at the bottom of B being stopped, the jacket B may be filled with warm water, say at 30° C.; a further depression of the surface of the mercury occurs. If the jacket be filled with water at a higher temperature, the mercury falls still further, and so with increase of temperature until the boiling-point is reached. At this stage, the jacket should be connected with the flask C, containing boiling water. The tube F is simply an escape valve for the surplus steam which bubbles through the water in D. On opening the spring clip E, steam passes through the jacket B, and the mercury descends until it becomes stationary at the same level in each limb of the U-tube. As the water in the tube is in this way heated by a current of steam from the flask C, it must be at the same temperature as is the steam. Under these circumstances, the mercury in the outer limb is subjected to the pressure of the atmosphere, that in the inner to the pressure of steam at the atmospheric pressure. The surface of the mercury in the two limbs being level with each other is a proof that the two pressures balance, and therefore **the boiling-point of water, or any other liquid, is that at which the tension or pressure of its vapour equals that of the atmosphere.** That the same holds good with any other liquid may readily be shown by substituting the liquid to be tested for the water in the above experiment.

Thus the flask c and the barometer tube may both be charged with alcohol, and again the tension of the vapour at its boiling-point will equal that of the atmosphere.

From this it follows that with variations in atmospheric pressure the temperature of the boiling point also varies. On the tops of mountains, the atmospheric pressure is low, and water boils considerably below 100° C. On the other hand, in steam boilers the pressure is very high, and the boiling-point rises; thus at a pressure of 4 atmospheres (60 lbs. per square inch) the temperature of the boiling-point is 144°, and at 150 lbs. per square inch rises to 180° C.

49. **Solution and Crystallisation.**—The powerful solvent action of water has been already mentioned. On solid bodies its solvent power usually increases with the temperature. Thus sodium sulphate is soluble in rather more than double its weight of water at ordinary temperatures, but dissolves easily in its own weight of warm water. This is not, however, an invariable rule, for common salt, NaCl, dissolves to the same extent in cold as hot water. With some liquids, as alcohol, water mixes, or is miscible, in any proportion, each being mutually soluble in the other. With other liquids, water is not miscible; thus if water be shaken with either oil or ether, the two separate from each other into different layers according to their specific gravity. In such a case the water is found to have dissolved a certain proportion of the ether, while also the ether has dissolved some of the water. Non-miscible liquids are therefore more or less soluble in each other. Gases dissolve in water in widely varying proportions, from traces only, with gases such as hydrogen, to many hundred volumes in the case of ammonia and allied gases. With gaseous bodies the degree of solubility diminishes with an increase of temperature, and, by continual boiling, water may practically be freed from any gaseous bodies held in solution.

Referring somewhat more fully to solid substances, their degree of solulibity varies very considerably. They may, however be divided into:

(1) Freely soluble substances as, sugar, washing soda, salt, alum.

(2) Slightly soluble substances, as plaster of Paris or gypsum.

(3) Insoluble substances, as chalk, flint, sand, barium sulphate.

Under similar conditions of temperature, &c., every substance has a specific degree of solubility; thus ordinary potash alum is at 15° C. soluble to the extent of 15·13 parts of the salt in 100 parts of water; the proportion gradually increases until, at 100° C., 357·48 parts of alum are dissolved by 100 parts of water. Such a solution containing as much of the salt as it can possibly dissolve is termed a *saturated* solution. Any more of the salt added remains unacted on, and if the solution be cooled a portion of the alum separates in the solid form; thus any saturated solution of alum at a higher temperature than 15 °C. will on being cooled to that point deposit solid alum, until it contains only 15·13 parts of alum to the 100 parts of water.

On examining the alum thus deposited, it is found to have assumed more or less regular geometric forms, which are termed crystals. The same applies to most other substances which are deposited in the solid state from a solution, as a result either of its cooling or evaporation. **Bodies are said to be crystalline when they consist of crystals; for chemical purposes a crystal may be defined as matter which has assumed during the act of solidification a definite geometric form. In crystals there is also a definite internal molecular arrangement related to the crystalline form by certain laws.** The same substance, as a rule, always crystallises in the same form, or group of closely allied forms. On the other hand some substances assume two or more distinct crystalline forms according to the conditions under which the crystals are produced; such substances are said to be *dimorphous*, or *polymorphous*, bodies. Any substance which is not in a crystalline condition is said to be *amorphous*, i.e. without (crystalline) form. The same substance at times occurs in either the crystalline or amorphous state, according to the conditions under which it has been formed. When various substances assume the same crystalline shape they are said to be *isomorphous* with each other.

Crystals have been classified into six systems, which may best be described by reference to the following figures :

I. Regular or Cubic System.—The first of this series, No. 14, is that of the regular octahedron: this figure, it will be noticed, has eight faces and six solid angles ; if each pair of

FIG. 14.

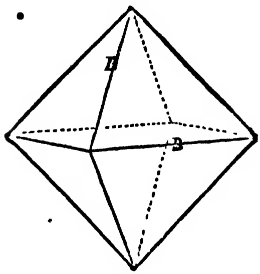
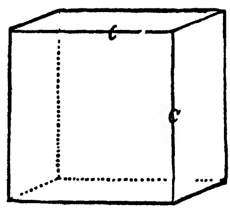


FIG. 15.



opposite angles be joined by an imaginary line, we shall have three lines of equal length, crossing each other in the centre, and all at right angles to one another. These imaginary lines are called *axes,* and in the regular system are all of them, as in the octahedron, equal in length and at right angles to each

FIG. 16.

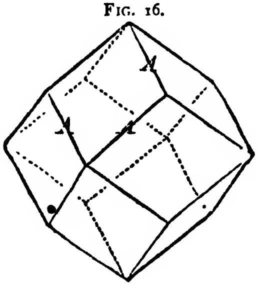
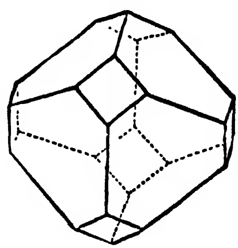


FIG 17.



other. The whole of the figures of the regular system may be referred to these axes. In the octahedron each face cuts all three axes ; in the cube, fig. 15, each face cuts one of the three and is parallel to the other two, or in other words cuts them at an infinite distance.

In fig. 16 we have the rhombic dodecahedron, in which

each face cuts two of the axes and is parallel to the third axis. Fig. 17 is an illustration of a frequent type of crystal composed partly of octahedral and partly of cubic faces. Alum, common salt, and fluor-spar are examples of substances which crystallise in the cubical system.

II. Tetragonal or Pyramidal System.—In this system there are again three axes, all at right angles, two of which are equal to each other, and the other, termed the primary or principal axis, either longer or shorter than the other two. Fig. 18 is an illustration of the octahedron (tetragonal pyramid) of this system. Potassium ferrocyanide, and tinstone (cassiterite) crystallise in the pyramidal system.

FIG. 18.

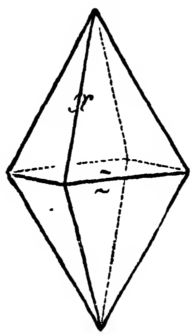
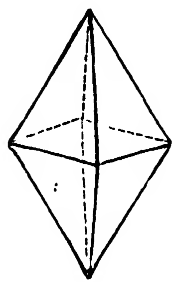


FIG. 19.



III. Rhombic System.—In this system the axes are all at right angles to each other, but all of different lengths; the simple pyramid or octahedron of this system is shown in fig. 19. Sulphur (when crystallising from solution) and zinc sulphate belong to the rhombic system.

IV. Monoclinic System.—The axes in this system are of unequal length; two of them are perpendicular and the third inclined to the plane of the other two. Gypsum, orthoclase, and cane-sugar crystallise in this system. The pyramid is illustrated in fig. 20.

V. Triclinic System.—This system is characterised by the three axes being of unequal length, and all obliquely placed with regard to each other. The pyramid of this system is

shown in fig. 21. Copper sulphate is one of the bodies crystallising in this system.

VI. Hexagonal System.—This system is distinguished from all the others by there being four axes. Three of these of

FIG. 20.

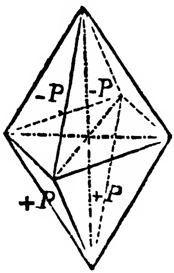
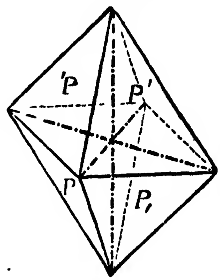


FIG. 21.



equal length are in one plane, and at angles of 60° from each other. The other, termed the principal or primary axis, is at right angles to the plane of the three, and may be of any length.

Fig. 22 is an illustration of a combination of a prism and pyramids of this system. The following figure shows the

FIG. 22.

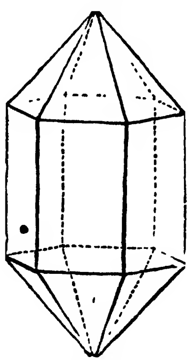
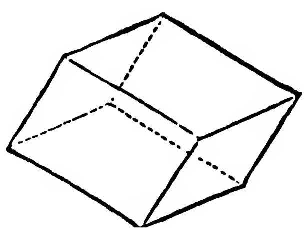


FIG. 23.



rhombohedron, another important form belonging to this system. Quartz, graphite, and calc-spar are examples of this system.

In the transition of crystalline substances from the solid to

the liquid state by solution, there is no intermediate stage; until the actual moment of solution, each crystal remains unaltered in physical characters. There is another class of bodies, whose behaviour with water is considerably different in character. One of the best examples of such bodies is ordinary gelatin, which body in its impure form is the glue of the carpenter. Dry glue is hard and brittle, and may be shivered in fragments by a blow with a hammer. If a few drops of water be added to a sheet of glue, it gradually permeates the whole mass, and slightly softens it. With the addition of more and more water, the glue becomes softer and softer, until at length it reaches the jelly-like consistency of the confectioner's jelly. Still further additions of water reduce this to a viscous liquid, which becomes more and more limpid as still further water is added. Such substances are not soluble in the ordinary sense of the term, but may rather be described as miscible with water in all proportions; there being no line marking the limit of saturation, as with crystalline bodies.

Substances possessing the jelly-like properties of gelatin are termed 'Colloids,' and do not acquire a crystalline form when assuming the solid state.—The colloid bodies are principally of organic origin; still there are some interesting examples among inorganic bodies, among which one of the most important is gelatinous silica, to be hereafter described.

50. Supersaturated Solutions.—Although there is a definite quantity of a salt which under, certain conditions, water is capable of holding in solution, yet there are certain circumstances under which, with some substances, this law is held in abeyance. For example, let a saturated solution be made of sodium sulphate at the boiling-point, and the filtered solution at 100° C. be placed aside in a clean flask. The usual rule would be that, as the temperature became lower, a continuous crop of crystals would be being deposited. But this solution, if free from solid particles, may be cooled down to the ordinary temperature without showing any signs whatever of a crystalline or other solid deposit. Such a solution is termed a super-

saturated solution, and so unstable is its equilibrium that the introduction of the smallest fragment of the solid sulphate starts crystallisation, and the whole excess of salt separates in the crystalline form within a few seconds. Pure water at times exhibits a somewhat similar phenomenon, for in clean flasks, when perfectly still, it may be cooled several degrees below the freezing-point without solidification; but any slight disturbance at once causes the production of ice, in well-marked crystalline form, and the whole mass becomes solid.

51. Water of Crystallisation.—Many bodies contain water as an essential constituent of their crystalline form. Thus crystals of the salt, sodium sulphate, to which reference has already been made, consist of ten molecules of water to one of the salt; this is thus represented in the formula, Na_2SO_4, $10H_2O$. On expelling this water by heat, the crystalline form is destroyed. On dissolving and re-crystallising tis anhydrous salt, it once more combines with its water of crystallisation. Reference has already been made to what is called dimorphism; the two distinct crystalline systems in which some substances occur are at times marked by differences in the quantity of water of crystallisation present. It must be understood that water is not an essential to crystallisation, as many substances form anhydrous crystals, among which are potassium chlorate and sodium chloride. Further there are other compounds which in crystallisation fulfil the same functions as water: among these alcohol is one of the most important, and many crystalline bodies contain alcohol of crystallisation.

52. Industrial Applications.—The first and foremost use to which water is put is its employment for potable and domestic purposes. Water required for these objects should be as pure as possible. The great essential in drinking waters is freedom from all sewage contamination; the presence of organic matter in large quantities, whether of animal or vegetable origin, is also most objectionable. These substances of themselves may not be positively injurious (although even that is doubtful), but are, in the case of the former, so generally associated with sewage matter that for that reason alone any

water containing more than the most minute traces of organic *matter is deservedly condemned for drinking purposes. Sewage-matter is not merely objectionable of itself, but still more so because it forms the vehicle by which cholera, typhoid fever, and other malignant diseases of similar character are propagated.* The presence of small quantities of saline matters, provided they are of inorganic origin, is not considered deleterious, although such bodies do not improve the water for potable purposes. The aëration of the water by carbon dioxide and oxygen gases imparts to it a brisk and pleasant flavour.

The other leading domestic purpose beside that of drinking, to which water is applied is that of washing. Waters which lather readily are termed soft; those which do not do so, but first destroy or curdle a quantity of soap are termed hard. Hardness is generally the result of the presence of compounds of calcium and magnesium, and is fully discussed in a subsequent chapter.

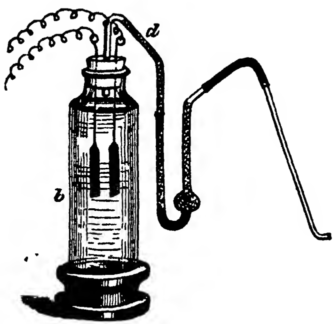
Water is used so widely in the manufactures that any detailed description of its uses is impossible. For industrial applications soft water is always preferable. Water is largely used in steam boilers, and for that purpose should be soft and free from acid or corrosive properties. Saline impurities cause a deposit of 'scale' during evaporation; and any corrosive action manifests itself by an attack on the metal of the boiler. For dyeing and other operations water must be largely employed; practically in all such applications it is its solvent power, combined with its chemical inactivity, which renders it so especially valuable.

53. Composition by Volume.—Until comparatively recently water was considered to be an element, but during the eighteenth century it was shown, by Cavendish, that the combination of hydrogen and oxygen in the proportions of two volumes of the former to one of the latter produces pure water, and pure water only. Lavoisier repeated Cavendish's experiments in 1783 and first deduced therefrom the true explanation of the composition of water.

It has already been shown, paragraph 38, that water may be

separated into oxygen and hydrogen by means of the intense heat of the electric spark. The passage of an electric current through water is the most convenient method of effecting its decomposition into its constituent gases. For this purpose, the apparatus sketched in fig. 24 may be employed. The apparatus consists of a wide-mouthed bottle, *b*, tightly fitted with an india-rubber cork. Through this cork is passed a leading tube *d*, filled with calcium chloride, in order to dry the evolved gases. There are also passed through the cork two platinum wires, to the lower ends of which are attached pieces of platinum foil (electrodes) so arranged that they face each other at a distance of about half an inch. These wires are connected with the poles of an electric battery consisting of from three to five Grove's or Bunsen's cells. The bottle is filled to the neck with water to which a few drops of sulphuric acid have been added, in order to increase its electrical conductivity. On the passage of an electric current, bubbles are seen to arise from each of the platinum electrodes, and the evolved gas may be collected from the leading tube over either mercury or water. When the gas is required in the dry state mercury must be employed. If a soda-water bottle be filled with the gas and then held to a flame, the gases recombine with a violent explosion: at the same time a film of moisture is deposited on the inside of the dry bottle.

FIG. 24.



Further information may be gained from a modified form of this experiment, in which the gas evolved from each of the electrodes is collected separately. One form of apparatus suitable for this purpose is that shown in fig. 25, in which V is a small trough containing the acidulated water. The electrodes are connected with the binding-screws S S, and over each is inverted a small glass jar, filled with acidulated water. On the

battery being connected by wires to the screws S S, bubbles of gas are seen to be evolved from each electrode, and are collected in the two small gas tubes. As the experiment proceeds the one tube is seen to fill at just twice the rate of the other. On examination it will be found that the more rapidly filled tube is that inverted over the electrode connected with the zinc or negative pole of the battery. On being tested, the double volume of gas is found to burn quietly on a light being applied, and is pure hydrogen : the single volume of gas rekindles a glowing splinter and is pure oxygen. In this way, the student learns that **water may be decomposed into two volumes of hydrogen and one volume of oxygen.** One circumstance about this experiment is at first somewhat puzzling, pure hydrogen is evolved at the one electrode, and pure oxygen at the other ; while there is no sign of any transference of gas from the one to the other electrode through the liquid. What, then, becomes of the oxygen which was in com-

FIG. 25.

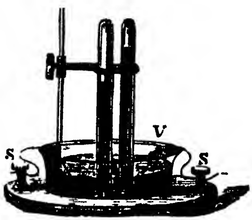
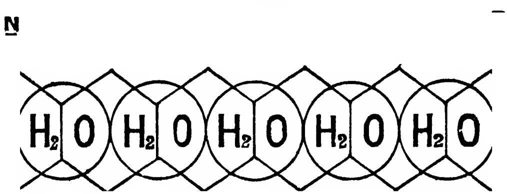


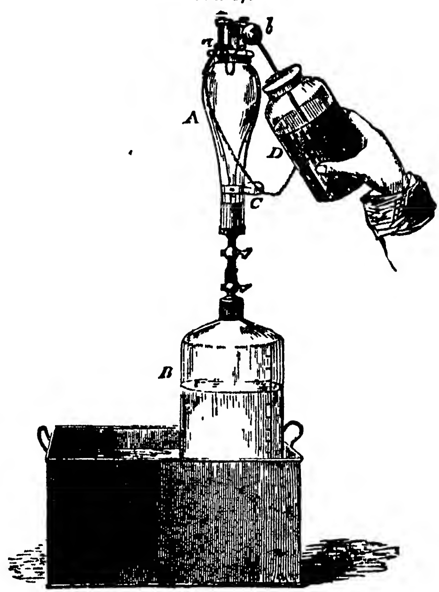
FIG. 26.



bination with the evolved hydrogen, and the hydrogen which was in combination with the evolved oxygen? This may best be explained by reference to the diagram given in fig. 26, in which N and P are portions respectively of the negative and positive electrodes of the apparatus shown in fig. 25. The series of circles by which these are connected are intended to represent a line of molecules of water, making complete con-

tact between the two electrodes. This is indicated by each containing the formula of water, H_2O. On the passage of an electric current, the molecule lying next to the negative electrode, N, is decomposed and its hydrogen liberated in the gaseous state: its oxygen combines with the hydrogen of the next molecule to form water, and its hydrogen in turn decomposes the next adjoining molecule until finally the molecule contiguous to the positive electrode, P, is reached, the oxygen there, finding no other molecule to decompose is set at liberty, and escapes in the gaseous form. The formation of this second series of molecules is indicated in the diagram by the series of hexagons shown. If the electrode P be formed of any readily oxidisable metal, such as zinc, the nascent oxygen combines with it to form an oxide, none escaping in the gaseous state.

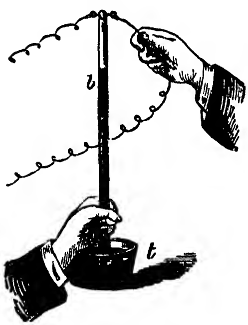
Fig. 27.



The experiment with the soda-water bottle full of the mixed gases, which explode on the application of a light, shows that the reunion of oxygen and hydrogen again produces water. Precisely the same effect is obtained if the bottle be one-third filled with oxygen and two-thirds filled with hydrogen prepared in any other manner. The passage of an electric spark through the mixture also effects their recombination. In connection with this, Cavendish's original experiment is of con-

siderable interest, the apparatus employed being shown in fig. 27. The vessel B is a graduated glass jar, standing in a pneumatic trough and filled with a mixture of pure hydrogen and oxygen in the proportions of two volumes to one. Attached to this, by means of a brass tube containing stopcocks, is a stout glass vessel, A, fitted with a tightly ground stopper, through which pass two platinum wires, *a*, arranged with their ends slightly apart. In use, the vessel A (known as Cavendish's eudiometer) is thoroughly cleaned and dried, and then exhausted by means of an air-pump; it is then screwed on to the jar B. The series of stopcocks C and the others are opened, when A at once fills with the mixed gases. The stopcocks are closed, and by means of the Leyden jar, D, an electric spark is passed through the mixture. The gases combine with a bright flash, and drops of water condense on the sides of the eudiometer. The stopcocks are again opened, the vessel refills, and a second quantity of water is produced by a repetition of the electric spark. This operation may be repeated until the whole of the mixed gases is used, by which time an appreciable quantity of water will have been accumulated in the eudiometer.

FIG. 28

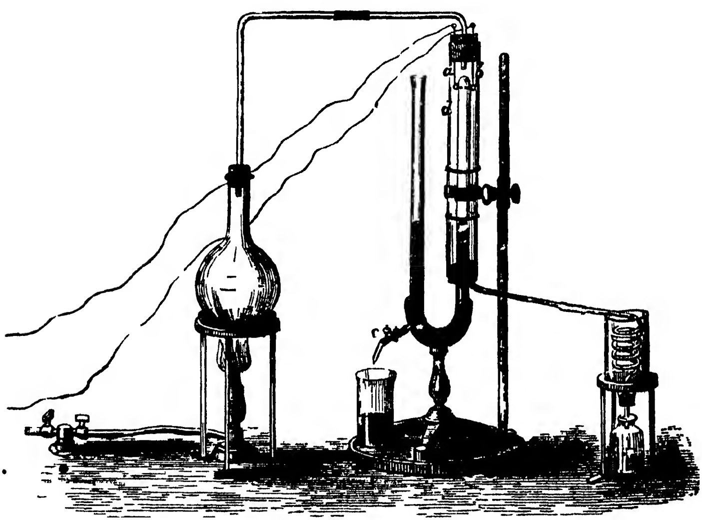


On a smaller scale the experiment may be performed with the simpler apparatus shown in fig. 28. The eudiometer in this case consists of a glass tube about half an inch in diameter, and some twenty inches in length, closed at one end. Near this end two platinum wires are fused through the substance of the glass. In use the eudiometer is filled with mercury, and then inverted in the little trough *t*, containing the same metal. The tube is about one-third filled with the mixed gases from the generating apparatus, fig. 24. An india-rubber pad is then slipped underneath its open end in the mercury trough, on which it is firmly held down; then, by means of the wires, an electric spark from an induction coil is passed through the mixture. Combination ensues, and on slightly raising the tube

from the pad, the mercury rushes up and entirely fills it, as the water formed almost immediately condenses.

A most important modification of this experiment is one in which the combination of the gases is effected at a temperature above the condensing point of steam. For this purpose the apparatus shown in fig 29 may be employed. The eudiometer is in the shape of a U tube, having its one end closed and a pair of platinum wires, *a b*, fused through it as before. This limb is enclosed in a jacket *d*, through which vapour of amylic

FIG 29

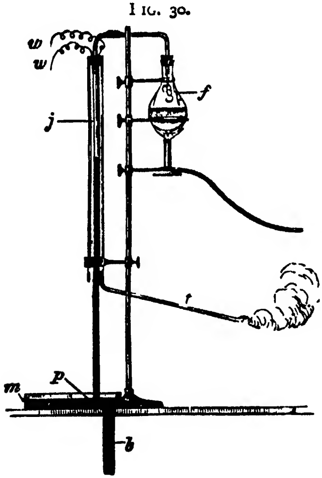


alcohol (boiling point, 132° C), or some other liquid boiling at a high temperature, is passed. This liquid is gently boiled in the glass flask shown, and the vapour condensed, after use, in the small worm shown to the right of the figure. The closed limb of the eudiometer having been filled with mercury, to the stopcock *c*, the amylic alcohol vapour is passed for some little time through the jacket. This is in order to see that it is perfectly dry, as otherwise the mercury would descend, owing to an accumulation of steam in the eudiometer. The results

of this test being satisfactory, some five or six inches of the eudiometer are filled with the mixed gases. Amyl-alcohol vapour is again passed, and mercury is withdrawn from *c* until the level is the same in both limbs of the eudiometer. The height is marked by an elastic band which slides over the tube *d*; the open end of the eudiometer is firmly closed with the thumb and an electric spark passed. The volume of the gas is seen to contract; mercury is added to the open limb until the two surfaces are again level, when as before the gas is at atmospheric pressure. Being thus measured under the same conditions of temperature and pressure, the gas is found to occupy just two-thirds its original volume.

An interesting modification of the apparatus for this experiment is that devised by Reynolds, and shown in fig. 30, in which use is made of the fact that water boils at a lower temperature under diminished atmospheric pressure. A straight eudiometer tube is employed, some thirty inches in length, its upper part being enclosed in the steam jacket. The mixed gases are inserted in this tube, which, filled with mercury, stands in the mercury trough *m*. The flask *f* contains water, and the steam therefrom passes through the jacket *j*. As the mixed gases are above a mercury column in the eudiometer, some twenty-four inches in height, they are under a very much diminished pressure—only about one-sixth that of the atmosphere. The result is that the boiling-point within the eudiometer is reduced to about 50 or 60° C., according to the exact height of the mercurial column. The volume of the gases is indicated by an elastic band outside *j*, and the height of the mercurial column is measured and noted. The eudiometer

FIG. 30.



being placed on an india-rubber pad *p*, an electric spark is passed and a diminution in volume of the gas noted. The end of the eudiometer is next placed within the well *b*, and depressed until the mercury column is of exactly the same height as before the explosion. In this way equality of temperature and pressure is secured at each time of measurement. The gas is then measured and is found again to be two-thirds its original volume. From these experiments we learn that **three volumes of the mixed gases, consisting of two volumes of hydrogen and one volume of oxygen, produce two volumes of steam measured at the same temperature and pressure.** This is expressed in the following equation in graphic form :—

$$\boxed{H_2} + \boxed{H_2} + \boxed{O_2} = \boxed{H_2O} + \boxed{H_2O.}$$

Two molecules of hydrogen. One molecule of oxygen. Two molecules of water.

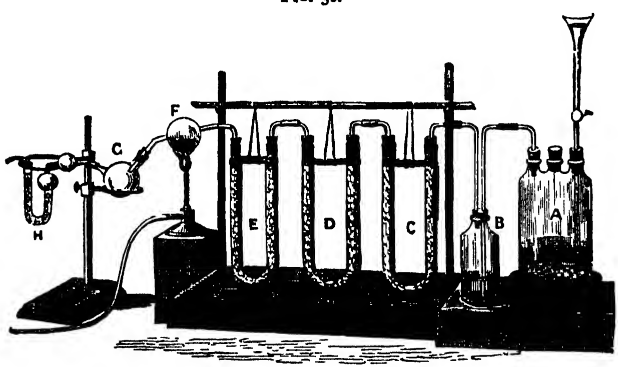
54. Composition by weight.—The composition by weight of water is one of the starting points in ascertaining the composition of other bodies, and so has been determined with the greatest possible accuracy. For this purpose use is made of the fact that if copper oxide be heated in a current of hydrogen, water is found according to the following equation—

$$\underset{\text{Copper oxide.}}{CuO} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Water.}}{H_2O} + \underset{\text{Copper.}}{Cu.}$$

For exactness it is necessary that the hydrogen be in a state of absolute purity; this is effected by a system of purification such as is shown in fig. 31, in which A is a Woulffe's bottle fitted for the generation of hydrogen from zinc and dilute sulphuric acid. The evolved gas is first passed through a wash-bottle, B, containing a solution of caustic potash, KHO, which retains any traces of sulphuric acid that may have been carried over mechanically. There is next a number of U-tubes, C, D, E, arranged so that the gas passes through the whole series. In C are placed fragments of pumice moistened with a solution of mercuric chloride, $HgCl_2$; this removes any traces of sulphuretted hydrogen. The next tube, D, is filled with small

pieces of caustic potash, which absorbs any traces of carbon dioxide gas that might be present, and also helps to dry the gas. The next tube, E, is filled with fragments of pumice moistened with sulphuric acid, and serves to thoroughly dry the gas. From E nothing but pure dry hydrogen should emerge. The bulb F is blown in difficultly fusible glass, and contains pure oxide of copper, which, after being heated to redness, is cooled in dry air. This bulb and its contents are carefully weighed. Attached to F is a bulbed receiver, G, and lastly a U-tube, H, containing fragments of calcium chloride. In use, hydrogen is generated in A, which after the expulsion of the whole of the air is connected with the purifiers, B, C,

FIG. 31.



D, E. The exact weight of the copper oxide bulb, and also that of G and H, are noted. Hydrogen is passed through the apparatus until the whole of the air is expelled throughout. The bulb F is then carefully heated, when the copper oxide is decomposed, with the formation of water. This collects in the bulb and calcium chloride drying-tube H. The reaction being over, the bulb F is allowed to cool, the wash-bottle B is disconnected, and air drawn through the apparatus until the hydrogen is displaced. The series F, G, H are then again weighed; the loss in weight of F represents the quantity of oxygen consumed; the gain in weight of G and H shows the amount of water passed. The weight of hydrogen is deter-

mined by the difference between the two. For determination of the most exact type other additional precautions are adopted and the various weighings made *in vacuo*. Dumas, to whom we are indebted for a most exact determination of the gravimetric composition of water, took such quantities of copper oxide as yielded him about 50 grams of water. As a result of 19 experiments Dumas found that 840·161 grams of oxygen were consumed in the production of 945·439 grams of water, from which the following percentage composition of water is deduced—

Oxygen	88·864
Hydrogen	11·136
	100·000

Or, if hydrogen be taken as the unit, 1 part of hydrogen by weight combines with 15·9608 parts by weight of oxygen.

55. **Osmose and Dialysis.**—There are certain chemical properties of bodies which may at this stage of the student's progress receive explanation. Among these are those whose names head this paragraph. The miscibility of liquids has already been explained : when such liquids as are miscible are placed in layers one on the other, so that the lighter of the two is on the top, they mix or diffuse one into the other more or less rapidly. **The diffusion of liquids may take place not only through a porous diaphragm, but also through certain non-porous substances of special physical character; such diffusion is termed Osmose.** Thus, although a bullock's bladder may be distended by air, and allowed to dry in that distended state without the air escaping, yet a piece of such bladder permits some aqueous solutions to pass through its substance with comparative readiness. Either animal parchment or so-called vegetable parchment-paper possesses, when wet, the same properties. If a short cylinder of glass, gutta-percha, or other impervious material be made into a shallow dish (proportioned somewhat like a tambourine) by fastening securely thereto a piece of parchment, an appliance is thus produced which well shows liquid diffusion. Let such

a dish be partly filled with saturated brine, and then floated in a vessel of pure water. After some hours the solution within will have diffused out through the membrane, carrying with it some of the salt in solution, until the water both outside and inside contains the same percentage of salt. By repeatedly changing the water in the outer vessel, the whole of the salt might be removed from within the parchment-bottomed cylinder. If this parchment drum were next filled with a solution of gum or gelatin, and the same experiment repeated, it would be found that the gum was incapable of traversing the membrane. If a mixture of brine and gum were placed in the parchment-drum and then floated on the surface of the water, the salt would diffuse out and the gum remain behind; in this way a complete separation of the two might be effected. Crystalline bodies generally share with salt the ability to pass through a membrane of this kind; the colloids cannot so pass when in solution. **The separation of bodies by their respective ability or inability, when dissolved, to pass through parchment-like membranes, is termed Dialysis.** Dialysis is at times a most useful method of separating bodies which otherwise are almost inseparable. Many of the changes and separations which occur in living organisms are due to osmose and dialysis.

56. Solids, Liquids, and Gases.—Water is perhaps the most familiar of all bodies with which we are acquainted in the three physical states of solid, liquid, and gas. It has been already shown in paragraph 47 that this difference of state is closely dependent on the heat-condition of the body. When **in the solid state the molecules of a body cohere together so closely and firmly that their separation or movement over one another is only effected with difficulty. In consequence, a piece of the body retains its own shape** not merely against the action of gravity, but also in most cases even when subjected to a considerable weight or pressure. With a sufficient weight some bodies thus alter their shape, without breaking; these are termed ductile bodies. Others, similarly tested, crush into fine fragments or

powder, and are known as brittle substances. All are, however, solids, and for further particulars of their classification according to physical characters, works on physics should be consulted.

Notwithstanding the rigidity of solid bodies, their molecules are nevertheless capable of minute movements within the mass of the substances, these movements being due to the action of heat. As the temperature of the substance is raised, a point is at last reached (varying for different bodies) at which the heat molecular movements overcome the cohesion due to the solid state, and the solid changes either into a liquid, or at times directly into the gaseous condition. In order to effect this change, a certain quantity of heat is necessary, and this heat is employed in doing the mechanical work of overcoming the molecular cohesion existing in the solid. Such heat is definite in amount, and does not raise the temperature of the body. **In the liquid state, the molecules of a body flow more or less readily over each other, but still possess a varying amount of coherence, and resist any attempt to pull them asunder,** although such resistance is feeble compared with that offered by solids. That it exists is readily shown by an experiment with a clean glass plate suspended horizontally from one arm of a balance. Let this plate be first counterpoised, and then floated on the surface of a dish of water. It will now be found that a considerable weight must be added to the pan on the other arm of the balance in order to pull the plate away from the water. That the resistance thus overcome is that of the cohesion of the water particles for each other is shown by the fact that the glass plate when pulled away is wet. A layer of water still adheres to the plate, and the severance has been between particles and particles of water. Those liquids in which the molecules flow over one another very readily—as, for example, ether—are remarkably mobile or limpid; others, as water, occupy a medium position, while some, as the various oils and syrups, flow only slowly, these latter are said to be viscous. Owing to this flowing property of liquids, under the influence of gravity, they adapt themselves to the shape of the vessel in which they are contained, being bounded with a level surface at the top. (Large volumes

of liquid, as seas or lakes, show sensibly the curvature of the earth.) In small drops of water, as dew-drops, the action of gravity is exceedingly small, compared with that of liquid coherence, and in consequence such drops are almost perfectly spherical. The same phenomenon is observed in isolated globules of mercury.

On further application of heat to liquids, a point is at last reached at which the motion imparted to the molecules is sufficient to overcome the cohesion still existing between them, and the liquid is changed into the gaseous condition. To effect this change a considerable quantity of heat is necessary, and this heat being occupied in doing mechanical work does not raise the temperature of the body. To change liquids into gases requires, as a rule, more heat than to convert the same substance into a liquid from the solid state. Thus to change 1 gram of water into steam requires 6·8 times as much heat as is necessary to convert 1 gram of ice into water. Bodies occupy in the gaseous state many times more volume than when in the liquid condition; thus, a cubic inch of water is roughly stated by engineers to produce a cubic foot of steam. **Gases are characterised by their molecules possessing no coherence, and by their expanding or contracting to exactly fill the space in which they are confined; they exhibit in the highest degree the properties of compressibility and elasticity.** These latter properties are best described after some explanation of the actual constitution of gases.

57. Kinetic Theory of Gases.—An earlier idea of the spontaneous expansion of a gas when the closed space containing it was enlarged, was that the molecules possessed a property of mutual repulsion; this is a view which is no longer tenable. It has already been explained that heat effects the change of a liquid into a gas, and that such a change is due to the motion imparted to the molecules on being heated. Energy which consists of active motion of matter is termed *kinetic* energy (from the Greek word 'I move'); on the other hand that dormant energy which exists, for instance, in a piece of coal, and is liberated or changed into active (kinetic) energy on its

being burned, is termed *potential* energy. According to the kinetic theory, each molecule of a gas moves in straight lines with a uniform velocity for the same temperature. When a molecule strikes against another or the walls of the containing vessel, it rebounds, according to the laws of mechanics which govern the behaviour of moving bodies.

58. Pressure and Volume of Gases.—It may readily be demonstrated by experiment that gases exert pressure. Thus if in the vacuous space at the top of a barometer, the minutest quantity of gas be inserted, the height of the mercury is immediately depressed, and such depression can only be due to the pressure exerted by the gas. Further the pressure which any gas exerts is dependent on the volume which it occupies. Thus, supposing a cubic foot of gas be contained within a cylinder supplied with a frictionless piston, and that it exerts a pressure equal to 15 lbs. on each square inch of surface of the piston and cylinder; let the piston be withdrawn from the cylinder sufficiently far to enlarge its cubic capacity to two feet; the gas will then be found to exert a pressure of 7·5 lbs. to the square inch. If, on the other hand, it be compressed to half a cubic foot, the pressure will be found to amount to 30 lbs. per square inch. It is understood throughout that the temperature is constant when the pressure is measured. From these data may be deduced the following law, known as that of Boyle and Marriott: **The volume of any gas is inversely proportional to the pressure to which it is subjected.** Minute variations from this law occur at temperatures not far removed from the liquefying point of any particular gas; but with this reservation it applies equally to all gases whatever their nature.

Let us see how this may be explained according to the kinetic theory. In the first place pressure itself is explained as being due to the impact on the surface of the containing vessel of the showers of these rapidly moving molecules. Each molecule delivers a blow on the surface, and as they are moving with uniform velocity, and the molecules are practically equally distributed throughout the containing space, the number of impacts

during each successive unit of time of equal force is constant. As the pressure is simply the sum of the force of each individual impact, there is consequently constant pressure. If the volume of the gas be doubled, the molecules are only half as closely packed, and as a result the unit of surface will only receive half the number of molecular blows within the unit of time. As the molecular velocity is unaltered, half the number of blows or impacts will produce only half the pressure.

As the volume of gases varies with the pressure to which they are subject, it becomes necessary to employ some standard of pressure to which are referred all measurements of gaseous volume. The most important source of pressure to which gases are subject is that of the atmosphere, of which the height of the mercury column of the barometer is a direct measure. For scientific purposes, the height of this column is usually expressed in millimètres (*m.m.*). **The standard pressure for the comparison of gaseous volumes is that which causes the barometer to stand at a height of 760 millimètres.**

59. Temperature and volume of Gases.—Not only does the volume of a gas vary with its pressure, but also with the temperature to which it is subject. Supposing one cubic foot of gas, enclosed within the cylinder fitted with piston before referred to, have its temperature increased. The piston will be forced out, as the volume increases, the pressure remaining the same; or if the piston be fixed the pressure will increase. In either alternative the increase of volume, or of pressure, as the case may be, will be in the same ratio: this follows from Boyle's law. Careful measurements have shown that, under constant pressure, one volume of a gas expands $\frac{1}{273}$ of its volume at 0° C. for each degree increase in temperature; therefore the coefficient of expansion of gases is said to be $\frac{1}{273}$ or 0·003665. Now if the mean or actual quantity of gas within a fixed space be the same, the only explanation of increase of pressure, according to the kinetic theory, is that the velocity of movement of the molecules must have suffered change. If the velocity of the rectilinear motion of the molecules be increased

then the pressure also increases. If the velocity of the molecule be doubled, the pressure is quadrupled, because not only does each molecule strike the unit of surface with double the force, but also there are double the number of blows struck within the unit of time. Hence the measure of kinetic energy is taken as half the product of the square of the velocity into the mass ($\frac{1}{2} m v^2 = k$); and the pressure which a gas exerts is proportioned to the sum of the kinetic energy of the molecular motion of the mass of gases. It has been found by experiment that, the density or volume of a gas remaining the same, its kinetic energy is proportioned to its temperature, reckoned from $-273°$ C. Now from this statement it follows that a gas would be devoid of kinetic energy at a temperature of $-273°$ C., and as kinetic energy is due to the heat-motion of a gas, **it is assumed that at $-273°$ C. bodies exhibit no heat-motion, or are devoid of heat. In consequence this point has been termed the absolute zero of temperature, and temperature reckoned therefrom is termed absolute temperature.** Starting from this assumption the expression for the relation between the volume of a gas and its temperature becomes very simple. **Under constant pressure the volume of a gas is directly proportional to its absolute temperature.** Owing to this variation in volume with temperature, **the temperature of 0°C. has been selected as the standard for the comparison of gaseous volumes.**

The term normal temperature and pressure is frequently applied to 0° C. and 760 *m.m.*, which are also indicated by N.T.P. used as an abbreviation.

60. Gaseous Diffusion.—The molecules of a substance in the gaseous state being in such active movement, it may readily be understood that gases rapidly mix or diffuse into each other. For instance, if in a large room a jar of chlorine be opened at the level of the floor, the presence of the gas may, owing to its powerful odour, be detected within a few seconds in every part of the room, notwithstanding that the chlorine is more than double the density of atmospheric air. **The natural process by which one gas is thus disseminated through**

another, is termed gaseous diffusion. It takes place through all gases even when the heavier is at first at the lower level, and proceeds until a uniform mixture is attained. Gaseous diffusion not only occurs with gases placed in contact, but also between gases separated by a thin partition of some porous material, as, for example, a thin diaphragm of plaster of Paris or porous earthenware. So that if a vessel be divided in two by such a diaphragm, and each portion be filled with a different gas, they gradually intermix as before, although not so quickly as when in absolute contact. The rate of diffusion of gases through such a diaphragm is not uniform, but depends on their densities; thus the heavier a gas the more slowly does it diffuse. This is readily proved experimentally, in the following manner: A piece of glass tubing some twelve inches in length, and an inch in diameter, has one end stopped with a plaster diaphragm. This is easily made by mixing a little plaster of Paris with water to the consistency of a thick cream, spreading the mixture on a plate to a depth of an eighth of an inch, and then pressing down in it the end of the glass tube, which must be allowed to remain undisturbed until the plaster has set. The tube is then set aside, and allowed to become dry. In order to fill it, the porous diaphragm is covered on the outside with tinfoil, and then the tube is filled with hydrogen by upward displacement. The inverted tube must next be transferred to a pneumatic trough, and placed on a shelf so that its end is about half an inch below the surface of the water. The tinfoil is then removed; the hydrogen diffuses outward through the diaphragm, and air diffuses inward. That the hydrogen diffuses more rapidly is proved by the fact that the water rises within the tube against the action of gravitation, until the tube is about two-thirds full of water. If, as a converse experiment, the tube be filled with carbon dioxide gas, which is of greater density than air, the inward diffusion is the more rapid, and the water is driven entirely out of the tube. As a result of experiments of this kind, with special precautions taken to avoid error, it is found that **the rate of diffusion of gases is inversely as the square root of their density.** Thus hydrogen, with a density of 1, diffuses four times as rapidly as oxygen with a density of 16.

Let us see how this is explained according to the kinetic theory of gases. At the same temperature, any two gases—for example, oxygen and hydrogen—exert the same pressure, provided the same number of molecules are enclosed within a unit of space. (This results from Avogadro's law, which is fully dealt with hereafter.) As the pressure is due to the impact of the molecules, it follows that the lighter molecules of hydrogen must be moving with greater rapidity than those of oxygen to produce the same amount of pressure by the sum of the impact of the molecules. According to the kine ic theory, equality of pressure arises from the equality of the kinetic energy of the motion of the molecules. Calling the mass of the oxygen molecule 16 and its velocity 1, and kinetic energy k, we have for $\frac{1}{2}\,mv^2 = k$ ..

$$\frac{16 \times 1^2}{2} = k = 8$$

As the pressure of the hydrogen is the same it follows in its case also that $k = 8$, and the mass of the molecule is 1 ; then $\frac{1}{2}\,mv^2 = k$ becomes

$$\frac{1 \times v^2}{2} = k = 8$$

$$\text{and } v^2 = \frac{8 \times 2}{1} = 16$$

$$v = 4$$

that is, the velocity of the hydrogen molecule must be four times that of the molecule of oxygen, in order to produce equal pressure. As the number of molecules which hit the bounding surface increases in the same ratio as the velocity, there must also be four times as many hydrogen molecules hit the unit of surface within the unit of time, as there are of oxygen. An investigation of the above equations shows that **the ratio of the velocity of the rectilinear movement of the molecules of different gases at the same temperature and pressure is inversely as the square roots of their densities. The number of molecular impacts on the unit of surface within the unit of time varies in the same proportion.** A simple proof of this fact may be obtained by

calculating the momentum ($m v$) in each case, in accordance with this law, and seeing whether they coincide. For oxygen, with n being the number of molecular impacts in the same space of time, we have

$$n m v = 1 \times 16 \times 1 = 16$$

For hydrogen we have—

$$n m v = 4 \times 1 \times 4 = 16$$

Thus, assuming that in the upper line of the following table the whole of the densities of the various gases are correctly given (chlorine is slightly in excess), the ratio of velocity and number of molecular impacts is shown in the lower.

	H_2	H_2O	O_2	Cl_2
Density	1	9	16	36
Velocity	6	2	1·5	1

But evidently it is the number of molecular impacts which govern the rate of diffusion, because if our unit of surface be converted into an aperture in an airtight partition between the two vessels of gas, the number of molecules which would have struck against that surface becomes the number which pass through or diffuse into the other gas. Therefore, **according to the kinetic theory, the rate of diffusion is directly as the number of molecular impacts on a unit of surface within a unit of time, and this number varies inversely as the square roots of the densities of different gases.**

Hydrogen Peroxide, or Hydroxyl.—Formula, H_2O_2. Molecular weight, 33·92. Specific gravity, 1·452.

61. Occurrence.—Minute traces of this body appear to exist in the air; in the various processes employed for the preparation of ozone, hydrogen peroxide is also produced in small quantities.

62. Preparation and Manufacture.—It has already been stated that the normal basic oxides form water as a secondary product when acted on by an acid. Certain of the peroxides, under somewhat similar conditions, produce hydrogen peroxide. Barium peroxide is one of the most suitable for this

purpose, and when suspended in ice-cold water to which an acid is added, yields the peroxide of hydrogen. The analogy between the basic and the peroxide is shown in the following equations :—

BaO	+	H_2SO_4	=	$BaSO_4$	+	H_2O.
Barium oxide.		Sulphuric acid.		Barium sulphate.		Water.
BaO_2	+	H_2SO_4	=	$BaSO_4$	+	H_2O_2.
Barium peroxide.		Sulphuric acid.		Barium sulphate.		Hydrogen peroxide.

This latter reaction is that which is usually employed for the preparation of this body both for laboratory purposes and also on the manufacturing scale. The barium peroxide is first prepared in the pure state and is then added to cold dilute sulphuric acid (1 of acid to 5 of water) until the acid is nearly neutralised. The solution is filtered from the precipitated insoluble barium sulphate, and the slight trace of acid remaining is removed by the addition of a solution of barium hydrate, BaH_2O_2, until the solution is neutral to litmus. There is thus produced an aqueous solution of hydrogen peroxide, which is concentrated by evaporation over sulphuric acid *in vacuo* until the water is evaporated.

In small quantities hydrogen peroxide may also be prepared by the passage of carbon dioxide gas through ice-cold water in which barium peroxide is suspended. It is interesting again to notice the reactions exhibited both by the normal oxide as well as the peroxide.

BaO	+	CO_2	+	H_2O	=	$BaCO_3$	+	H_2O.
Barium oxide.		Carbon dioxide.		Water.		Barium carbonate.		Water.
BaO_2	+	CO_2	+	H_2O	=	$BaCO_3$	+	H_2O_2.
Barium peroxide.		Carbon dioxide.		Water.		Barium carbonate.		Hydrogen peroxide.

In the first of these reactions the water takes no part, but in the second the nascent oxygen of the barium peroxide attaches itself to the molecule of water, forming hydrogen peroxide.

63. **Properties.**—In its most concentrated form, hydrogen peroxide is a liquid of oily consistency, transparent and colour-

less, devoid of smell, and having a metallic astringent taste. It bleaches litmus and many other organic colouring matters. As shown by its formula, the peroxide is water with another atom of oxygen contained within the molecule. This extra atom is held with very little tenacity, for the concentrated liquid decomposes slowly even at low temperatures; at 20° C. bubbles of oxygen may be seen escaping, and at higher temperatures oxygen is evolved with great rapidity. A very short time of boiling is sufficient to entirely decompose the peroxide, with the escape of oxygen, leaving only water.

$$\underset{\text{Hydrogen peroxide.}}{2H_2O_2} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}.$$

The presence of a small quantity of free sulphuric acid renders the concentrated liquid less prone to decomposition, while the peroxide in the dilute state, especially if slightly acid, is fairly stable.

Hydrogen peroxide is a powerful oxidising agent, and, for instance, changes sulphurous into sulphuric acid, and lead sulphide into lead sulphate.

$$\underset{\substack{\text{Sulphurous}\\\text{acid.}}}{H_2SO_3} + \underset{\substack{\text{Hydrogen}\\\text{peroxide.}}}{H_2O_2} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} + \underset{\text{Water.}}{H_2O}.$$

$$\underset{\substack{\text{Lead}\\\text{sulphide.}}}{PbS} + \underset{\substack{\text{Hydrogen}\\\text{peroxide.}}}{4H_2O_2} = \underset{\substack{\text{Lead}\\\text{sulphate.}}}{PbSO_4} + \underset{\text{Water.}}{4H_2O}.$$

It also decomposes potassium iodide by a reaction similar to that occurring with ozone; the free iodine, being recognised by its action on starch, serves as a test for hydrogen peroxide. If the test be made in the presence of ferrous sulphate, $FeSO_4$, the reaction still occurs, while other oxidising agents produce under such conditions no reaction.

Another oxidising action of this body serves also as a means for its detection in small quantities. If a liquid containing hydrogen peroxide be acidulated with sulphuric acid, and then some ether and a drop of solution of potassium bichromate, $K_2Cr_2O_7$, added, and then shaken, the ether on again rising to the surface is found to be of a deep blue colour. The colouration is due to the oxidation of the chromium com-

pound to perchromic acid, which gives to the ether its blue tint.

Hydrogen peroxide behaves in what seems at first sight a somewhat anomalous manner with the oxides of silver, gold, and one or two other metals. If washed silver oxide be added to a solution of hydrogen peroxide, oxygen gas is rapidly evolved, and the silver oxide reduced to the metallic state, the peroxide at the same time being reduced to water—

$$\underset{\text{Hydrogen peroxide.}}{H_2O_2} + \underset{\text{Silver oxide.}}{Ag_2O} = \underset{\text{Water.}}{H_2O} + \underset{\text{Silver.}}{2Ag} + \underset{\text{Oxygen.}}{O_2}.$$

In this peculiar reaction, hydrogen peroxide acts apparently as a reducing rather than an oxidising agent. Silver oxide, in common with those of the other noble metals, is a body in which the oxygen is held but feebly. We have, therefore, the condition that a loosely-attached atom of oxygen exists in both the peroxide and the silver oxide; the attraction of the oxygen atoms for each other is greater than that for the other bodies with which they are at the time united, and so they combine to form a molecule of oxygen.

More difficult of explanation is the fact that finely divided silver, gold, and platinum also possess the power of causing a violent decomposition of hydrogen peroxide without themselves undergoing any alteration.

64. **Industrial Applications.**—The bleaching properties of hydrogen peroxide have led to its somewhat extensive use as a hair bleacher, dark-coloured hair being changed by its action to a light flaxen tint. Its oxidising power on lead sulphide has also been pressed into service. The basis of most oil colours is white lead—lead carbonate. In pictures this white body gets slowly more or less changed into lead sulphide, which is black, by the action of sulphur compounds in the air. Such old, discoloured pictures may, in great measure, have their colour restored by treatment with hydrogen peroxide, which by conversion of the lead sulphide into lead sulphate again produces a white body.

CHAPTER V

CHLORINE AND HYDROCHLORIC ACID

Chlorine.—Symbol, Cl. Atomic weight, 35·37. Density, 35·37. Specific gravity, 2·435. Molecular weight, Cl_2, 70·74. Melting-point, −102° C. Boiling-point, −33·6° C. at atmospheric pressure.

65. **Occurrence.**—This gas is not known in the free state in nature, but occurs in vast quantities in combination with sodium, forming rock salt.

66. **Preparation.**—The gas may be readily obtained from its compound with hydrogen (hydrochloric acid, HCl), by the action of manganese dioxide; on mixing these substances together a compound of chlorine with manganese is formed thus:—

$$\underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Manganese dioxide.}}{MnO_2} = \underset{\text{Manganese tetrachloride.}}{MnCl_4} + \underset{\text{Water.}}{2H_2O.}$$

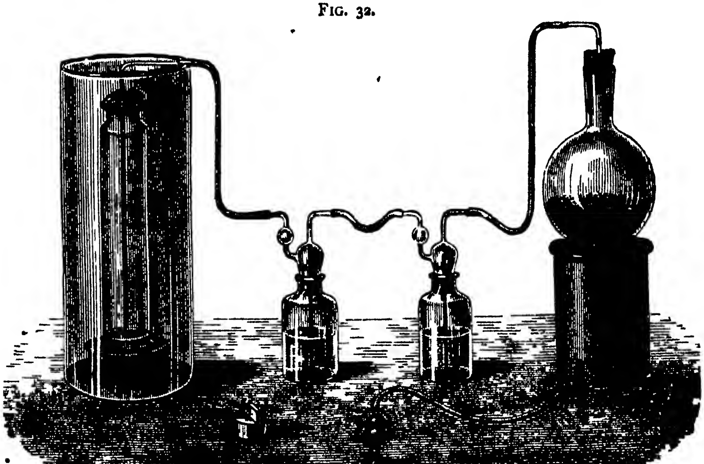
The manganese tetrachloride is an unstable compound, and, with an elevation of temperature, is decomposed into a chloride containing half the amount of chlorine, with the separation of the remainder in the free state:—

$$\underset{\text{Manganese tetrachloride.}}{MnCl_4} = \underset{\text{Manganese dichloride.}}{MnCl_2} + \underset{\text{Chlorine.}}{Cl_2.}$$

In the actual preparation of the gas these two actions go on together, the tetrachloride being decomposed as rapidly as formed. Chlorine is manufactured in large quantities by this process for various uses in the arts. The apparatus used in the laboratory is shown in figure 32, in which on the right-hand side is shown a flask in which the manganese dioxide and hydrochloric acid are heated together. It is preferable to use the dioxide in the form of small lumps, about the size of peas, rather than the fine powder commonly employed. The gas is passed through two wash-bottles, the first containing water, by

which traces of hydrochloric acid are removed; and the second, concentrated sulphuric acid, which acts as a drying agent. The gas is next collected by downward displacement in a dry jar arranged over a powerful down-draught fitted to the table, and enclosed in a large cylinder of glass in order to catch the chlorine as it escapes from the gas jar. The solubility of chlorine necessitates its being collected either by displacement or over warm water. This reaction is the most convenient for ordinary laboratory purposes, but chlorine is sometimes prepared from common salt (sodium chloride) direct, by the action

FIG. 32.



on it of manganese dioxide and sulphuric acid; the gas is disengaged in the cold, but more rapidly with the application of heat. The whole of the chlorine is liberated :—

$$\underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Manganese dioxide.}}{MnO_2} =$$

$$\underset{\text{Hydrogen sodium sulphate.}}{2NaHSO_4} + \underset{\text{Manganese sulphate.}}{MnSO_4} + \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Water.}}{2H_2O.}$$

Chlorine may also be obtained by the electrolysis of a solution of hydrochloric acid.

67. Manufacture.—Chlorine is so largely used for various purposes that its manufacture constitutes a most important branch of chemical industry. As just mentioned, the reaction between manganese dioxide and hydrochloric acid is largely employed for this purpose. On the manufacturing scale, large stills are constructed of Yorkshire flags, with the edges cemented together with vulcanised india-rubber, and having a capacity of about 200 gallons. The lower parts of these stills are steam-jacketed, and into them are introduced hydrochloric acid of sp. gr. 1·160 to 1·170 (a waste product of the manufacture of sodium carbonate from sodium chloride) and manganese dioxide in small lumps. The reaction which occurs is similar to that which takes place on a smaller scale, when the gas is prepared for laboratory purposes.

Weldon's Process.—An important improvement in the manufacture of chlorine is that known as Weldon's process, in which the manganese is recovered from the waste of the chlorine stills in such a form as enables it to be again used. The acid still liquid is neutralised by the addition of calcium carbonate in excess in the form of chalk or marble, any iron and alumina present are thus also removed by precipitation. The impurities are allowed to subside, and the liquid solution of chlorides of manganese and calcium is mixed with calcium hydrate, CaH_2O_2, in excess. This mixture being heated to from 55° to 75° has a brisk current of air blown through it. By a somewhat complicated reaction the manganese is peroxidised, and precipitated as a thin black mud (Weldon's mud), having the approximate composition, $CaMnO_3,H_2MnO_3$. Analysis of this formula shows that this body may be viewed as containing $2MnO_2,CaO,H_2O$: the whole of the manganese is therefore completely oxidised to its original state of deoxide. This regenerated oxide is used for the manufacture of chlorine as before described; it is much more easily attacked than the native oxide, and requires less hydrochloric acid to produce the same amount of chlorine.

Deacon's Process.—On the passage of air and hydrochloric acid through a heated chamber, a partial decomposition of the acid occurs, with the production of water and free

chlorine. If this chamber be filled with fragments of brick which have been saturated with a solution of copper sulphate, the decomposition of the hydrochloric acid occurs much more readily, although the copper sulphate itself undergoes no chemical change. Deacon utilises this reaction commercially by causing the mixture of hydrochloric acid and air escaping from salt-cake furnaces (see manufacture of sodium carbonate) to pass into chambers containing the sulphated brick fragments, heated to about 420° C. When in thorough working order, about 60 per cent. of the hydrochloric acid is thus converted into chlorine, according to the equation—

$4HCl$	$+$	O_2	$=$	$2H_2O$	$+$	$2Cl_2$.
Hydrochloric acid.		Oxygen.		Water.		Chlorine.

68. Properties.—Chlorine is a gas of a yellowish-green colour, possessing a most pungent and disagreeable odour, which when much diluted with air somewhat resembles that of sea-weed. When in the pure state, or even moderately concentrated, it acts as an irritant poison, rapidly attacking the mucous membrane of the respiratory organs. Water at a temperature of 15° C. dissolves 2·368 volumes of the gas, producing a solution resembling the gas in odour and colour. At 0° C. a pressure of six atmospheres reduces the gas to a liquid; while at a temperature of −34° the gas condenses at ordinary pressures. It solidifies at −102° C. to a mass of yellow crystals.

Chlorine, like oxygen, is a supporter of combustion and is non-inflammable. Its range of combustion-supporting power is not, however, exactly parallel with that of oxygen. Both elements combine readily and vigorously with hydrogen; but while oxygen also combines almost as energetically with carbon, carbon is incombustible in chlorine. In most cases where bodies burn in chlorine, combustion commences at a lower temperature than in oxygen. On exposing a mixture of hydrogen and chlorine to diffused daylight, the gases slowly combine, while either bright sunlight, or that of burning magnesium wire, causes their immediate union, with explosion. Phosphorus, on being plunged unlighted in chlorine, first

melts and then takes fire, burning with a faintly luminous flame. Finely divided antimony, arsenic, or copper in the form of thin foil (Dutch metal, which is an alloy of copper and zinc, answers the purpose) all take fire when introduced into chlorine. The powerful attraction of chlorine for hydrogen causes the decomposition of many compounds of carbon and hydrogen (hydro-carbons). Thus if tow, or other similar substance, be dipped in turpentine, $C_{10}H_{16}$, and then plunged into a jar of chlorine, combustion ensues, with the formation of hydrochloric acid, and the separation of the carbon in the free state. It will be seen that many of these reactions with chlorine occur spontaneously, and, as a rule, a lower temperature is sufficient to induce the commencement of the formation of chlorides, although the heat evolved during combination is less than that liberated in the production of the corresponding oxides. The following table of equations shows the formation of a number of chlorides :—

$$\underset{\text{Hydrogen.}}{H_2} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Hydrochloric acid.}}{2HCl.}$$

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Chlorine.}}{10Cl_2} = \underset{\text{Phosphorus pentachloride.}}{4PCl_5.}$$

$$\underset{\text{Antimony.}}{2Sb} + \underset{\text{Chlorine.}}{5Cl_2} = \underset{\text{Antimony pentachloride.}}{2SbCl_5.}$$

$$\underset{\text{Turpentine.}}{C_{10}H_{16}} + \underset{\text{Chlorine.}}{8Cl_2} = \underset{\text{Hydrochloric acid.}}{16HCl} + \underset{\text{Carbon.}}{10C.}$$

$$\underset{\text{Sodium.}}{2Na} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Sodium chloride.}}{2NaCl.}$$

In connexion with the Deacon process it has been pointed out that the oxygen of atmospheric air can effect the decomposition of hydrochloric acid, with the liberation of chlorine. Under other conditions, chlorine is able to effect the decomposition of water, with the liberation of oxygen. This change slowly occurs if a solution of chlorine in water be exposed to the sun's rays, and can be readily observed by inverting a gas jar filled with the solution in a small trough also containing water saturated with chlorine. As the decomposition occurs, bubbles of oxygen

accumulate over the chlorine water in the gas jar. At higher temperatures the same reaction occurs more rapidly, and if a mixture of steam and chlorine be passed together through a red-hot porcelain tube, the escaping gases are found to contain oxygen in considerable quantity, which may be collected in the pneumatic trough over cold water. The reaction is thus represented :—

$$\underset{\text{Chlorine.}}{2Cl_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Oxygen.}}{O_2}.$$

69. **Industrial Applications.**—Chlorine is manufactured in enormous quantities for the purpose of bleaching calico and other goods. For convenience of application it is usually stored as a combination of chlorine and lime to be hereafter described, and known commercially as chloride of lime. Chlorine also forms a most valuable disinfectant.

Bleaching.—The natural colour of calico is familiar, as 'unbleached calico' is largely used for purposes where purity of colour is not an object. If perfectly dry calico be immersed in dry chlorine, no action occurs, but in the presence of moisture the colour rapidly disappears. The change is due to the fact that the chlorine combines with the hydrogen of the water, and the nascent oxygen thus produced attacks most vegetable colouring matters, oxidising them into compounds almost or entirely devoid of colour. Litmus, indigo, and most other vegetable colouring matters are thus attacked ; so also is ordinary writing ink, which is a compound of salts of iron with organic acids. Printer's ink, which is composed of finely divided carbon mixed with oily matter, is not thus changed.

Hydrochloric Acid.—Formula, HCl. Molecular weight, 36·37. Density, 18·18. Specific gravity, 1·2474. Melting-point, −112·5° C. Boiling-point, 10° C. under a pressure of 40 atmospheres.

70. **Occurrence.**—At ordinary temperatures hydrochloric acid is a gas, and is found in small quantities in the gaseous mixture evolved from volcanoes. This compound has also received the name of muriatic acid (from *muria*, brine), and is

the only known compound of hydrogen and chlorine. Its preparation by the direct union of these elements has already been described.

71. Preparation.—The gas is easily obtained by the action of sulphuric acid on almost any chloride; because of its cheapness, common salt, NaCl, is usually employed. Salt in its ordinary form is so finely divided that the action proceeds with almost unmanageable rapidity. This may be modified by first fusing the salt and then breaking the solid mass thus obtained into small lumps. The gas is extremely soluble in water, and therefore has to be collected by downward displacement.

The reaction is represented by the following equation:—

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{NaCl} = \underset{\substack{\text{Hydrogen}\\\text{sodium sulphate.}}}{NaHSO_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl.}$$

One atom of the hydrogen of the sulphuric acid is here driven out by the sodium. At a much higher temperature than could be used with a glass flask, the second atom of hydrogen is displaced:—

$$\underset{\substack{\text{Hydrogen sodium}\\\text{sulphate.}}}{NaHSO_4} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{NaCl} = \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl.}$$

72. Manufacture.—Enormous quantities of solution of hydrochloric acid are obtained as a bye-product in the manufacture of sodium sulphate (salt cake), which operation is described in Chapter XXII. and illustrated in fig. 67. The process of manufacture is simply a repetition on the large scale of that described in the preceding paragraph. From a furnace in which the decomposition of the sodium chloride by sulphuric acid is effected, large volumes of hydrochloric acid escape. These are conveyed by the flue *d* (fig. 67) to the condensing towers E and F. These are brickwork structures filled with fragments of coke or brick, and having a stream of water descending through them from *h*, *h*. This water meets the upward current of hydrochloric acid gas, dissolves it, and the solution escapes at the bottom. In this way commercial aqueous hydrochloric acid is manufactured.

73. Properties.—Hydrochloric acid is a colourless gas which is rendered visible on coming in contact with air containing moisture, by the production of dense white fumes, consisting of a compound of the gas with water, which condenses to the liquid state. It has a sharp pungent odour, and when dissolved in water, a very acid taste. The gas is neither inflammable nor a supporter of combustion. At 10° C. a pressure of 40 atmospheres condenses this gas to a colourless liquid, and at −115° this liquid condenses to the solid state, re-melting at −112·5° C. Liquid hydrochloric acid does not appear to be a very active body, and exerts very little action on most of the metals. It is necessary to distinguish carefully between a liquid gas and a solution of the gas. Invariably in this work a liquid gas—as, for instance, 'liquid hydrochloric acid'—means the gas reduced by cold or pressure, or both, to the liquid state; a solution of the gas, as 'a solution of hydrochloric acid,' is the gas dissolved in water, unless some other solvent is specifically mentioned.

74. Aqueous Hydrochloric Acid.—This name is applied to the solution of hydrochloric acid gas in water. On opening the mouth of a jar of the gas under water, the jar is immediately filled; the first few drops of water absorb large quantities of the gas, and thus create a vacuum into which the water rushes with considerable force. At 4° C. water absorbs 492 volumes of hydrochloric acid, and the resultant liquid has a density of 1·2265. The aqueous acid thus prepared fumes strongly on exposure to air, and has the pungent odour of the gas. On being heated it evolves gaseous hydrochloric acid in large quantity until the liquid acquires a density of 1·100, when it distils over unchanged; this density does not, however, represent any constant of chemical composition, but varies with the atmospheric pressure under which the distillation is conducted. The acid exerts no bleaching action, but reddens litmus, and forms compounds with the metals termed chlorides on being brought into contact with their oxides. The aqueous acid is readily decomposed by iron, zinc, or other readily oxidisable metals, with the evolution of free hydrogen.

Gaseous hydrochloric acid is also decomposed in a manner similar to water when passed over red-hot iron filings. Commercial hydrochloric acid is commonly of a yellow colour, due to the presence of iron. Arsenic, salt, sulphurous and sulphuric acids, and free chlorine are also frequently present as impurities, The following table shows the strength of hydrochloric acid of various densities.

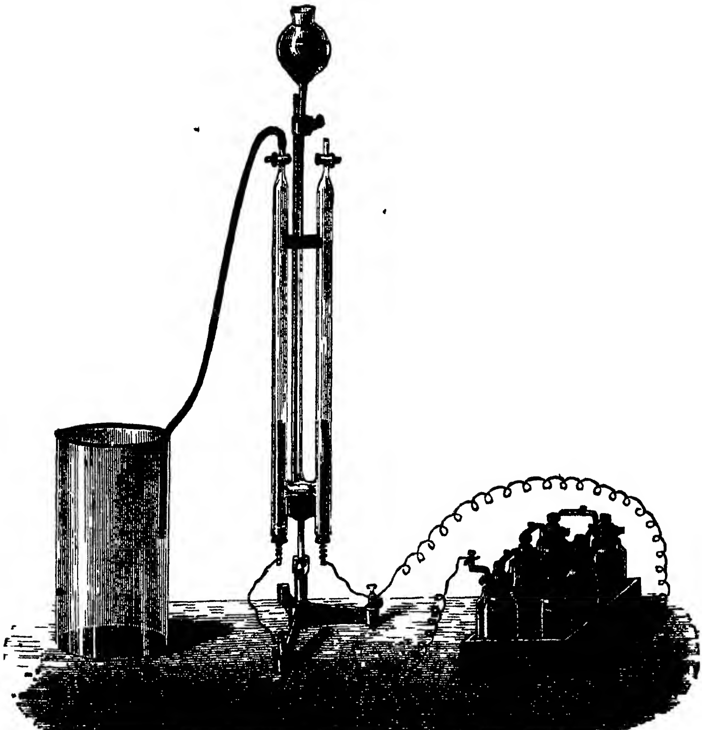
Density	Hydrochloric acid in 100 parts		Density	Hydrochloric acid in 100 parts	
	at 0° C.	at 15° C.		at 0° C.	at 15° C.
1·000	0·0	0·1	1·125	23·6	24·8
1·014	2·7	2·9	1·143	27·0	28·8
1·029	5·5	5·8	1·157	29·7	31·2
1·044	8·4	8·9	1·166	31·4	33·0
1·060	11·4	12·0	1·175	33·0	34·7
1·075	14·2	15·0	1·185	35·1	36 8
1·091	17·2	18·1	1·195	37·1	39·0
1·108	20·4	21·5	1·205	39·1	41·2
			1·212	41·7	42·9

75. Industrial Applications.—The impure commercial hydrochloric acid is largely used for the preparation of chlorine; also for the formation of chloride of tin, $SnCl_2$, a salt employed by the dyer and calico-printer. Ammonium chloride, NH_4Cl (sal-ammoniac) is manufactured in large quantity by treating the ammoniacal liquors of the gas-works with hydrochloric acid.

76. Composition.—That hydrochloric acid contains hydrogen and chlorine is readily shown by subjecting it to electrolysis. As nascent chlorine attacks and dissolves platinum, it is necessary to substitute electrodes of carbon for those of that metal. A suitable apparatus for the purpose is shown in fig. 33, which consists essentially of three glass tubes connected together at the lower end. The carbon electrodes are fitted to corks which pass through the open ends of two of the tubes; these tubes are fitted at the top with glass stopcocks. The third tube is provided with a bulb, and serves as a reservoir for the liquid displaced by the accumulation of gas. The apparatus is filled to the level of the opened stopcocks

with pure concentrated hydrochloric acid, and then connected with the voltaic battery. Hydrogen and chlorine are evolved respectively from the two electrodes, but as chlorine is soluble, it becomes necessary to continue the current until the liquid in the one limb is saturated with the gas. During this time

FIG. 33.



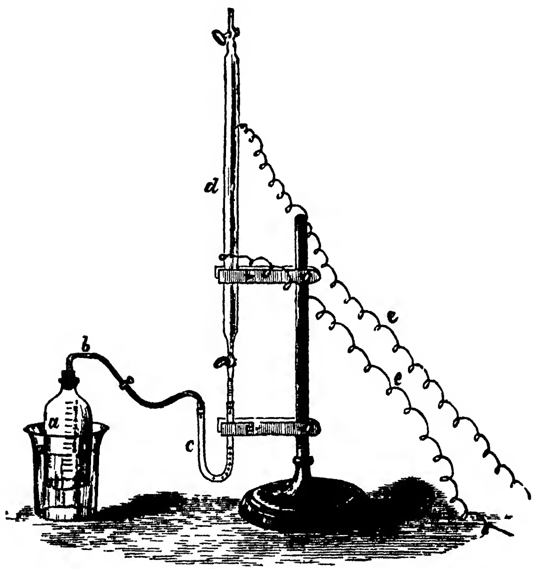
its colour gradually becomes yellow, through the absorption of chlorine. At this stage, on closing the stopcocks, gases accumulate in each limb in equal volumes; the one gas being found to be chlorine, and the other hydrogen.

It should be noted that chlorine, like oxygen, is liberated from the electrode connected with the copper or platinum

element of the battery. The following eight elements are alike in this respect, and from their behaviour on their compounds being subjected to electrolysis, are termed negative elements: oxygen, chlorine, bromine, iodine, fluorine, sulphur, selenium, and tellurium.

The experiment just described shows that the decomposition of hydrochloric acid yields hydrogen and chlorine in equal volumes, but it does not show the relation between the quantity

FIG. 34.



of hydrochloric acid decomposed and elementary gases liberated. Information on this point is gained from the following experiment.

A specially prepared tube, *d*, fig. 34, is obtained, having a stopcock at each end, and two platinum wires fused through the sides, so as to permit of an electric spark being passed between the ends. The jar *a* is filled with a mixture of chlorine and hydrogen in equal volumes, and on opening the stopcocks and spring clip, the mixed gases pass first through the drying-

tube *c*, and then fill the tube *d* by displacement. The stop-cocks are then closed, and an electric spark passed; combination ensues, and the resultant hydrochloric acid is permitted to cool. On now opening one of the stop-cocks under the surface of a trough of mercury, there is no escape of gas, neither does the mercury rise in the tube, consequently no alteration in volume has occurred. On opening the stopcock of the tube over water, the whole of the gas is dissolved with great rapidity. Therefore, **one volume of hydrogen and one volume of chlorine unite to form two volumes of hydrochloric acid gas.** Determinations of the densities of hydrogen and chlorine show that they are represented by 1·00 and 35·37 respectively; therefore, by weight, hydrochloric acid gas has the following composition:—

	Parts by weight	Percentage
Hydrogen	1·00	2·75
Chlorine	35·37	97·25
	36·37	100·00

CHAPTER VI

LAWS OF CHEMICAL COMBINATION BY WEIGHT AND VOLUME

77. Chemical Equivalents.—In connexion with the definitions of atoms and molecules given in the first chapter, it is explained that combination between elements always occurs in definite proportions. The chemistry of hydrogen chlorine and oxygen, and their compounds, having afforded several illustrations of such definite combinations, the laws of combination in definite proportion may at this stage be examined more closely and systematically. In the first place let us state the composition of the compounds already studied, together with gravimetric expressions of certain of the chemical changes which have been explained.

1 part of hydrogen combines with 7·98 parts of oxygen o form water.
1 ,, ,, ,, 15·96 parts of oxygen to form hydrogen peroxide.
1 ,, ,, ,, 35·37 parts of chlorine to form hydrochloric acid.

35·37	parts of chlorine	displace	7·98	parts of oxygen from water, with the formation of hydrochloric acid.
32·45	,, zinc	,,	1	part of hydrogen from hydrochloric acid.
27·95	,, iron	,,	1	part of hydrogen from hydrochloric acid.
27·95	,, ,,	,,	31·50	parts of copper from copper chloride, and at the same time—
27·95	,, iron	combine with	35·37	parts of chlorine.
31·50	,, copper	,,	15·99	parts of sulphur.
7·98	,, oxygen	and	99·90	parts of mercury are obtained by the decomposition of mercury oxide.

So far, these statements only refer to chemical reactions already described; to these may be added a few others that will further serve to illustrate the matter under consideration. First, let us take a series of displacement reactions, similar to that of iron on copper chloride.

99·90	parts of mercury	are displaced by	31·50	parts of copper from mercury chloride.
31·50	,, copper	,, ,,	27·95	parts of iron, from copper chloride.
31·50	,, ,,	,, ,,	32·45	parts of zinc from copper chloride.

In the next place, a well-known property of chlorine is that it displaces bromine and iodine from bromides and iodides, including those of hydrogen (hydrobromic and hydriodic acids).

35·37	parts of chlorine	displace	79·75	parts of bromine from hydrobromic acid.
79·75	,, bromine	,,	126·53	parts of iodine from hydriodic acid.

In the three compounds, hydrochloric, hydrobromic, and hydriodic acids, 1 part of hydrogen is combined respectively with 35·37 parts of chlorine, 79·75 parts of bromine, and 126·53 parts of iodine. From the statements just given the following deductions may readily be made:—

(1). 1 part of hydrogen may combine with, or be displaced from a compound by

7·98	parts of oxygen.
35·37	,, ,, chlorine.
32·45	,, ,, zinc.
27·95	,, ,, iron.
79·75	,, ,, bromine.
126·53	,, ,, iodine.

(2).	7·98 parts of oxygen 35·37 „ „ chlorine 79·75 „ „ bromine 126·53 „ „ iodine	May each replace the other in certain chemical compounds.
(3).	99·90 parts of mercury 31·50 „ „ copper 27·95 „ „ iron 32·45 „ „ zinc	May replace each other, or 1 part of hydrogen, in certain compounds.

The weights here given are said to be equivalent to each other in these various compounds. As hydrogen is here represented by 1, it is taken as the standard for comparison of the others, and accordingly, **the weight of an element which combines with, or by displacement expels from a compound, one part by weight of hydrogen, is termed its 'chemical equivalent.'** In passing, let it be carefully noted that the chemical equivalents are simply expressions of the results of actual experimental determinations; they are in no way dependent on any chemical theory or hypothesis.

78. Combination in Multiple Proportions.—The oxides of hydrogen, water and hydrogen peroxide, afford examples of two elements combining in more than one proportion. It will be observed that in the one compound exactly double the quantity of oxygen is combined with 1 of hydrogen as there is in the other. Taking other series of compounds into consideration, it is found throughout that a very simple relation exists between the proportions of each element found in the various compounds. In fact, **not only does chemical combination invariably occur in definite proportions, but also, when two elements happen to combine in more than one proportion, they unite in multiple proportions.** It may seem strange that this law was not discovered earlier in the history of chemistry than it was, but if the composition of bodies be expressed simply in percentages instead of being represented by formulæ, the fact is not so evident. To give an example, there are two compounds of carbon and oxygen which have respectively the following percentage compositions :-

	No. 1	No. 2
Carbon	42·857	27·273
Oxygen	57·143	72·727
	100·00	100·00

On the surface there is here no evidence of combination in multiple proportion ; 42 is no simple multiple of 27, neither is 72 of 57. But let us in each case see what weight of oxygen is combined with one part by weight of carbon : this is determined by dividing the weight of oxygen by that of carbon in each compound :—

$$\text{No. 1.} \quad \frac{57{\cdot}143}{42{\cdot}857} = 1{\cdot}33 \text{ of O to 1 of C.}$$

$$\text{No. 2.} \quad \frac{72{\cdot}727}{27{\cdot}273} = 2{\cdot}66 \text{ of O to 1 of C.}$$

When stated in this manner it is at once seen that to the unit of carbon there is twice as much oxygen in the latter compound as in the former.

Combination in multiple as well as in definite proportion is readily and consistently explained by the atomic theory ; the atoms have definite weight, and all compounds contain a whole number (and usually a comparatively small whole number) of atoms, consequently the proportional weight of each element present must either be the atomic weight or some multiple of the atomic weight.

79. Avogadro's Law.—When molecules are in the unaggregated or gaseous state, they follow laws of combination by volume, which are equally definite with those which govern combination by weight. As an introduction to these the student should again carefully read the 57th and following paragraphs which deal with the kinetic theory of gases and the relations existing between their volume, temperature, and pressure. Following on these an endeavour will now be made to explain a series of deductions on which a most important chemical and physical law is based.

In the first place if any two gases be taken for purposes of comparison, let it be remembered that the pressure is due to the kinetic energy of the motion of the molecules, and that if

the two gases be under similar conditions of temperature and pressure the kinetic energy of molecular motion is equal in each case. If two sets of molecules, whose mass is different be enclosed within the same vessel, they come to a state of equilibrium by a mutual exchange of energy, until the average kinetic energy of a single molecule of either gas is the same. Assigning to the gases the numbers 1 and 2, and as before calling mass, m, and velocity, v, we have

$$m_1 v_1^2 = m_2 v_2^2,$$

that is to say, the molecular momentum, mv^2, and kinetic energy, $\frac{1}{2}mv^2$, are equal.

Next a quantitative estimation of the pressure of the gas must be obtained. From the previous definitions, the pressure of a gas is evidently the molecular momentum multiplied by the number of molecules impinging on the unit of space in the unit of time. Calling the number of molecules n, we have

$$P = n m v^2,$$

but as the pressure is exerted in all directions, that exerted on one plane only, p, is represented by

$$p = \tfrac{1}{3} n m v^2.$$

Let us next suppose that our two gases are at the same temperature and pressure. In the first place it is a condition of equality of temperature that $m_1 v_1^2 = m_2 v_2^2$. Then the pressure being equal, we have $p_1 = p_2$, and

$$p_1 = \tfrac{1}{3} n m v^2 \text{ and } p_2 = \tfrac{1}{3} n_2 m_2 v_2^2.$$

But as $p^1 = p_2$, then

$$n_1 m_1 v_1^2 = n_2 m_2 v_2^2.$$

And as the temperatures are equal

$$m_1 v_1^2 = m_2 v_2^2,$$

and consequently,

$$n_1 = n_2.$$

In other words, **when any two gases are at the same temperature and pressure, the number of molecules in the**

unit of volume is the same in both gases. This law is known as that of Avogadro, being so named after its first discoverer. In its earlier history it was more of the nature of a hypothesis, and was accepted because of the consistent explanation of a number of chemical facts; but with the acceptance of the kinetic theory of gases, it is, as seen, capable of direct deduction from that theory. Another mode of statement of Avogadro's law, which is of importance to the chemical student, is the following: **At the same temperature, and under the same pressure, the volume of any gaseous molecule is the same, whatever may be the nature and composition of the gas.**

80. Constitution of Molecules.—The greater activity of hydrogen and oxygen in the nascent state has been adduced as proof that these elements normally exist as molecules containing more than one atom of the element. The law of Avogadro enables us to obtain proof of the same fact in another manner. Let us compare, for instance, the gases hydrogen and hydrochloric acid. Equal volumes under similar conditions have respectively the relative weights of 1·00 and 18·18; and by Avogadro's law the relative weights of the molecules must also be the same, because such equal volumes contain the same number of molecules. By experiment we know that hydrochloric acid contains half its volume of free hydrogen; consequently, as the molecular volume of hydrogen and hydrochloric acid is the same, there must be in the hydrochloric acid molecule half the amount of hydrogen contained in the molecule of hydrogen gas. In other words the molecule of hydrogen contains double as much hydrogen as the molecule of hydrochloric acid which occupies the same volume. Now the hydrochloric acid molecule must contain at least one atom of hydrogen, and, as only one atom has ever been obtained from it, we further conclude that it contains only one atom. Therefore the hydrogen molecule, which contains twice as much, must consist of two atoms, and no more than two, of hydrogen. The number of atoms in the molecule can only be determined in the case of those elements which can be measured and weighed in the gaseous state.

81. Combination by volume.—Knowing the molecular constitution of gases, it is easy to express the law by which their volumetric combinations are regulated. It is first necessary to express the particular chemical change by equations in which each gaseous element present is expressed by its molecular formula. Then, **the proportions by volume of all gaseous bodies which participate in any chemical reaction are in the direct ratio of the number of molecules of each body**; or, in other words, each molecule of a gas represents a unit of volume of that body. This is easily demonstrated by means of a few examples; in the following equations the molecule is represented by two squares, indicating that the volume is double that of an atom:

$$\boxed{H_2} + \boxed{Cl_2} = \boxed{HCl} + \boxed{HCl}$$

$$\boxed{H_2} + \boxed{H_2} + \boxed{O_2} = \boxed{H_2O} + \boxed{H_2O}$$

$$\boxed{H_2} + \boxed{H_2} + \boxed{H_2} + \boxed{N_2} = \boxed{NH_3} + \boxed{NH_3}$$

The first two reactions are already familiar to the student as those representing the formation of hydrochloric acid and water from their elements: the third represents the production in the same manner of NH_3, known as ammonia.

82. Determination of Atomic Weights.—It is only comparatively recently that even an approximate estimate of the *absolute* weight of atoms has been possible. For chemical purposes, however, the *relative* weights of atoms of different elements is of far more importance, and these have been determined with the greatest possible exactitude, every precaution known to chemical experimental science having been taken in order to ensure accuracy. In the first place some element must be selected as the standard of comparison, and both hydrogen and oxygen have been suggested for that purpose. As the atomic weight of oxygen is the fundamental one from which all others are calculated, it has been proposed to take it as the standard, calling its atomic weight 1, 10, or 100. Hydrogen, however, possesses the great advantage that its

atomic weight is less than that of all other elements and consequently, if it be taken as unity, all other atomic weights will be whole or mixed numbers. At the present time chemists are unanimous in their selection of the hydrogen standard, and accordingly **the atomic weight of hydrogen is taken as unity (1·00).**

Practically the first experimental step taken in the determination of the atomic weight is that of ascertaining the chemical equivalent of the element. This may be done by direct analysis or synthesis of its hydrogen compound, such as has been described in the case of water, or some other definite and well-marked chemical compound of the body is examined and its equivalent thus deduced. Thus, knowing that 7·98 is the chemical equivalent of oxygen, the quantity of any other element equivalent to that weight of oxygen might also be considered as equivalent to 1·0 part of hydrogen. For example, in determining the atomic weight of carbon, Dumas and Stas burned graphite, diamond, and charcoal in pure oxygen. They found that 1·375 grams of diamond (C), yielded 5·041 of carbon dioxide (CO_2), and consequently must have combined with 3·666 grams of oxygen. The chemical equivalent of carbon, in terms of that of oxygen, is in carbon dioxide therefore :

$$\text{As } 3{\cdot}666 : 7{\cdot}98 :: 1{\cdot}375 : 2{\cdot}99 \text{ of carbon.}$$

The chemical equivalent of silver has been many times determined with the greatest care, because it forms the starting-point in making other atomic weight determinations. Dumas burned finely divided silver in a current of chlorine gas and found that 107·97 parts of silver combined with 35·37 parts of chlorine to form silver chloride (AgCl).

The chemical equivalent may be identical with the atomic weight, but is not necessarily so : for example, when 1 part by weight of hydrogen combines with 7·98 parts of oxygen to form water, it does not follow that the combination is between one atom of each element. It may be that one atom of hydrogen has united with one of oxygen, or two atoms of hydrogen with one of oxygen, or the atoms may have combined in some other proportion. If the first supposition be correct,

the atomic weight of oxygen is 7·98, and the formula of water, HO ; if the second is the correct hypothesis, the formula must be H_2O, and the atomic weight of oxygen $7·98 \times 2 = 15·96$. It is evident, however, that the chemical equivalent must bear some simple relation to the weight of the atom ; it is, in fact, either identical or else an aliquot part of it. In deciding the atomic weight from the chemical equivalent the chemist is guided by the following considerations :—

(1) The density of the element and its compounds in the gaseous state.

(2) The specific heat of the element in the solid state.

(3) The crystalline form assumed by the compounds of the element.

These three methods must now be examined in detail.

(1) The density of the elements and their compounds in the gaseous state. The gaseous density of the element in certain cases agrees with the atomic weight, as deduced from other considerations, and always bears a simple relation to it. The following table gives the density of the gaseous form of those elements capable of being vaporised at manageable temperatures.

Name of Element	Density of gaseous form	Atomic weight
Hydrogen	1	1
Oxygen	15·96	15·96
Nitrogen	14·01	14·01
Chlorine	35·37	35·37
Bromine	79·75	79·75
Iodine	126·53	126·53
Sulphur	31·98 (at high temps.)	31·98
Selenium	78·00 (at high temps.)	78·00
Potassium	39·04 (?)	39·04
Sodium	22·99 (?)	22·99
Mercury	99·90	199·80
Cadmium	55·80	111·60
Zinc	32·45	64·90
Arsenic	149·80	74·90
Phosphorus . . .	61·92	30·96

Knowing from Avogadro's law that the molecular volume of all gaseous bodies is alike (similar conditions of temperature

and pressure are always understood), the weight of the molecules must be twice the density in terms of hydrogen as unity. For example, chlorine has a density of 35·37, and a molecular weight of 70·74. By a similar train of reasoning to that by which the molecule of hydrogen is shown to consist of two atoms, it may be shown that that of chlorine also contains two atoms, and therefore the weight of each atom must be 35·37. This number agrees with the chemical equivalent, and has been assigned as the atomic weight of chlorine.

With oxygen the density is just double the chemical equivalent (in water), and it is necessary to decide whether 7·98, or some multiple of that number, shall be taken as the atomic weight. Now water is capable of decomposition by the displacement of its hydrogen by sodium, and this displacement can take place in two distinct steps, one-half the hydrogen being displaced at a time: the obvious inference is that there are two atoms of hydrogen in water, that the formula must be written H_2O, and that $7·98 \times 2 = 15·96$ must be taken as the atomic weight of oxygen. This view receives further support from the proportions of combination by volume of oxygen and hydrogen—two volumes of hydrogen combine with one volume of oxygen to form two volumes of water (in the gaseous form), and hence the assumption that two molecules of hydrogen have combined with one molecule of oxygen to form two molecules of water. As two molecules of water contain between them two molecules of hydrogen, each water molecule must contain two hydrogen atoms, and therefore the molecular formula is required to be written H_2O.

In the case of mercury, cadmium, and zinc, the molecular weight, as determined from the density, is identical with the atomic weight, from which it follows that the molecules each contain but one atom, or are monatomic. Bearing in mind that the chemical definition of an atom is that it is the smallest possible particle that has been caused to enter into, or be expelled from, a compound, we deduce the atomic weight of mercury in the following manner. Its chemical equivalent is 99·90, that of oxygen being 7·98, but as the chemical equivalent of oxygen has to be doubled in order to give the weight of the

atom, that of mercury must also be similarly multiplied in order to give the atomic weight of mercury, 99·90 = 199·80.

Arsenic and phosphorus are distinguished by their density being double their atomic weight, and consequently their molecular weight quadruple that of the atom. Their molecules contain 4 atoms, and are termed tetratomic. The least possible quantity of phosphorus contained in any compound yet examined is 30·96, and so this number is selected as the atomic weight.

Not only does the molecular weight of elements as determined in the gaseous state afford assistance in the determination of the atomic weight, but so also do the molecular weights of their gaseous compounds. If we examine a series of such compounds, and determine the weight of the element in each, there cannot be less, of course, than an atom of the element present. And if the number of compounds be very large it may be assumed that some of them at least will contain no more than one atom, hence the rule: **The atomic weight of an element may be said to be the least weight of that element ever found in the quantity of any of its volatile compounds which occupies the same volume as two parts by weight of hydrogen**—that is, the weight found in the molecular volume of the substance. This method has the advantage of being applicable to elements themselves incapable of volatilisation. An example will make this more clear, and for that purpose carbon shall be chosen, being an element never obtained in the gaseous state.

Volatile compounds of Carbon	Molecular weight deduced from density	Weight of Carbon contained in the molecule
Carbon monoxide, CO . . .	27·93	11·97
Carbon dioxide, CO_2 . . .	43·89	11·97
Methyl hydride, CH_4 . . .	15·97	11·97
Acetylene, C_2H_2 . . .	25·94	23·94
Carbon chloride, CCl_4 . . .	153·45	11·97
Chloroform, $CHCl_3$ . . .	119·08	11·97
Methyl alcohol, CH_3HO . .	31·93	11·97
Ethyl alcohol, C_2H_5HO . .	45·90	23·94
Cyanogen, C_2N_2 . . .	51·96	23·94
Hydrocyanic acid, HCN . .	26·98	11 97
Carbon disulphide, CS_2 . .	75·93	11·97

An inspection of this series of compounds shows that in the molecular weight of each the quantity of carbon is represented by either 11·97, or a multiple of that number. An investigation on these lines confirms 11·97 as the atomic weight of carbon.

(2) **The specific heat of the element in the solid state.**—From a number of measurements of specific heat of the elements, Dulong and Petit, so early as 1819, arrived at the conclusion that **the specific heats of the elements in the solid state are inversely proportional to their atomic weights.** In consequence, if the specific heats of the elements be multiplied by their atomic weights, a series of numbers are obtained which theoretically should be identical. Practically, they, for a large number of the elements, closely approximate to each other. A direct deduction is that **the atoms of all elementary bodies possess the same specific heat.** While, in a large number of cases, Dulong and Petit's law is comparatively closely obeyed, yet some of the elements show very great discrepancies. These are firstly accounted for by the fact that the specific heat of the elements varies with the temperature, the two usually increasing together. Further, from the necessities of the case, the specific heat of some elements must be determined much nearer their melting-points than is that of others. The three principal exceptions to Dulong and Petit's law are carbon, boron, and silicon—elements closely resembling each other in chemical character, and all marked by a very low specific heat at ordinary temperatures. In order to test this question of the influence of temperature, the specific heat of carbon has been determined at temperatures varying from -80 to 1060° C. Above a certain temperature the specific heat becomes constant and follows the law of Dulong and Petit. The following table gives the specific heat of the most important of the elements in the solid state.

Name	Specific Heats	Temperature of observation	Atomic Weight from Specific Heat	Atomic Specific Heat
Lithium	0·941	+ 64°	Li = 7·01	6·6
Boron, crystalline	0·230	+ 36°	B = 10·9	2·5
„ „	0·366	+ 233°		4·3
„ „	0·5 (?)	+ 600°		(5·45)
Carbon, diamond	0·1318	+ 33·4°		1·58
„ „	0·3026	+ 247°		3·63
„ „	0·459	+ 985°	C = 11·97	5·5
Sodium	0·293	− 14°	Na = 22·99	6·7
Magnesium	0·245	+ 36°	Mg = 23·94	5·9
Aluminium	0·202	+ 37°	Al = 27·0	5·5
Silicon, crystalline	0·1697	+ 21·6°		4·75
„ „	0·203	+ 232°	Si = 28	5·7
Phosphorus, yellow	0·189	+ 19°	P = 30·96	5·9
Sulphur, rhombic	0·178	+ 67°	S = 31·98	5·7
Potassium	0·166	+ 34°	K = 39·03	6·5
Calcium	0·170	+ 50°	Ca = 39·9	6·8
Chromium	0·100	+ 36°	Cr = 52·4	5·2
Manganese	0·122	+ 55°	Mn = 54·8	6·7
Iron	0·112	+ 31°	Fe = 55·9	6·3
Cobalt	0·107	+ 55°	Co = 58·6	6·3
Nickel	0·108	+ 55°	Ni = 58·6	6·4
Copper	0·0930	+ 35°	Cu = 63·2	5·9
Zinc	0·0932	+ 33°	Zn = 64·9	6·1
Arsenic, crystalline	0·0814	+ 55°	As = 74·9	6·1
Selenium, crystalline	0·0840	+ 42°	Se = 78·9	6·6
Bromine, solid	0·0843	− 51°	Br = 79·76	6·7
Molybdenum	0·0722	+ 55°	Mo = 95·9	6·9
Palladium	0·0593	+ 55°	Pd = 106·2	6·3
Silver	0·0560	+ 36°	Ag = 107·66	6·0
Cadmium	0·0542	+ 37°	Cd = 111·7	6·0
Tin	0·0548	+ 34°	Sn = 117·4	6·5
Antimony	0·0523	+ 31°	Sb = 120	6·3
Iodine	0·0541	+ 59°	I = 126·53	6·8
Tellurium	0·0475	+ 36°	Te = 126·3	6·0
Platinum	0·0325	+ 36°	Pt = 194·3	6·3
Gold	0·0324	+ 55°	Au = 196·2	6·4
Mercury	0·0319	− 59°	Hg = 199·8	6·4
Lead	0·0315	+ 34°	Pb = 206·4	6·5
Bismuth	0·0305	+ 34°	Bi = 207·5	6·3
Uranium	0·0277	+ 49°	U = 240	6·6

It will be seen that the atomic specific heat, or specific heat of atomic weight of the elements in most cases falls between 6·0 and 6·5 and averages about 6·3. In a few elements the atomic specific heat is lower, while in some it rises as high as 6·8 and 6·9. It has already been explained that the temperature

and proximity to the melting-point must affect these determinations; in addition to these, the presence of unavoidable impurities, and errors of experiment, are disturbing causes. It may be possible, after the elimination of these sources of error, that specific heat determinations may not give absolutely identical atomic specific heats for the elements. And yet, Dulong and Petit's law may still be strictly true: the specific heat, as determined by experiment, is really occupied in producing two distinct effects: the first is that of raising the temperature of the body; this is true specific heat; the second is in causing the expansion of the body and producing other changes in the molecules of the element. If it were possible to determine the true specific heat as just defined, Dulong and Petit's law might absolutely apply.

The specific heat of atoms is apparently unaltered by chemical combination; that is to say, the molecule of a solid compound possesses a specific heat which is the sum of the specific heats of its component elements. Thus lead iodide, PbI_2, and bromide, $PbBr_2$, possess specific heats which are the sum of those of the constituent atoms. By subtracting the specific heat of the lead atom from that of the molecules of the compound, a result is arrived at, for the bromine and iodine respectively, which closely agrees with those obtained by direct experiment. The same course of investigations has been applied to the chloride, $PbCl_2$, and from it the atomic specific heat of chlorine has been calculated, the result being 5·95, which number agrees with the specific atomic heats of the other elements. The following gaseous elements have also been examined in the same way and with the following results:—

	Atomic Weights	Specific Atomic Heats
Hydrogen	1·0	2·3
Oxygen	15·96	4·0
Chlorine	35·37	5·95
Fluorine	19·1	5·0
Nitrogen	14·01	5·0 to 5·5

The three latter elements are thus brought fairly into agreement with the solid elements; hydrogen and oxygen are excep-

tions, but, if they follow the same rule as the carbon group, it is possible that examination of their compounds at very high temperatures may give atomic specific heats more nearly approaching the normal. The agreement between the atomic weights as deduced from the molecular volumes by Avogadro's law, and those obtained according to the law of Dulong and Petit, is a matter of deep interest. The student will remember that in the gaseous state the equal increments of temperature produce equal increments of kinetic energy; in the solid state equal increments of heat (at certain temperatures of comparison) produce equal increments of temperature in the atoms.

The great value of Dulong and Petit's law in the present state of chemical science is not so much the exact determination of the atomic weight, as the control of the chemical equivalent obtained by other methods. Thus zinc has a chemical equivalent of 32·45; its compound with chlorine consists, according to analysis, of

Zinc	32·45	by weight
Chlorine	35·37	„ „
Zinc chloride	67·82	„ „

If 32·45 be taken as the atomic weight of zinc, then the formula of zinc chloride would have to be ZnCl, that is it would consist of an atom of Zn weighing 32·45, and one of chlorine weighing 35·37. Let us see what information can be gained by the application of Dulong and Petit's law. The specific heat of zinc is 0·0932, and the average specific atomic heat is about 6·2. Calling the unknown atomic weight x, then we know that

$$0{\cdot}0932 \times x = \text{about } 6{\cdot}2$$

$$\text{and} \quad x = \frac{6{\cdot}2}{0{\cdot}0932} = 66{\cdot}5 \text{ approximate atomic weight of}$$

zinc. This number evidently does not agree with 32·45, but approximates to $32{\cdot}45 \times 2 = 64{\cdot}90$. This latter number is accordingly taken as the atomic weight, and the formula of zinc chloride must be taken as $ZnCl_2$, 64·9 of zinc being in combination with 70·74 of chlorine.

(3) The crystalline form assumed by the compounds of the element.—The meaning of the term isomorphism has already been explained as consisting of two substances crystallising in one and the same form. For example, certain somewhat complex sulphates exist which are termed alums; the best known of these is represented by the formula $AlK(SO_4)_3,12H_2O$. Now in this body the aluminium may be replaced by either iron (Fe) or chromium (Cr), without altering the crystalline form of the body. The assumption is that the replacement is atom for atom, and the weight of iron, 55·9, which replaces the weight of aluminium present, 27·3, is taken as the atomic weight of iron. This agrees with the figure obtained by the application of Dulong and Petit's law. The law of isomorphism, as discovered by Mitscherlich, may be expressed thus:— **The atomic weight of an element is that quantity which can, without changing the crystalline form, replace an atom of another element in a compound or series of compounds.** This law is not, however, absolutely trustworthy, for totally different substances are known which crystallise in the same form, and closely analogous bodies exist which crystallise in different forms; further, even the same substance may be dimorphous. It is principally as a confirmatory test that this law of isomorphism is employed.

83. **Molecular weights.**—It is impossible to determine with accuracy the molecular weights of any other compounds than those obtainable in the gaseous state. Thus for zinc chloride we may write $ZnCl_2$, and find that the composition thus expressed agrees with that determined by analysis of the body; but in reality the formulæ Zn_2Cl_4 or Zn_3Cl_6 would equally agree with the results of analysis. Molecular formulæ of bodies only known in the solid state may be taken as representing the simplest possible formula of the compounds, but the molecules themselves may be multiples of these simplest formulæ. The probability is that in very many instances they are such multiples. The principal guide to the selection of molecular formulæ for these solid compounds is that of

analogy. Thus ferric and aluminic chlorides are volatile, and from their densities the molecular formulæ of Fe_2Cl_6 and Al_2Cl_6 are deduced. The chloride of chromium is very similar in certain of its characters, and so is known by the formulæ $Cr_2 Cl_6$. It is important, then, to remember that in our present state of knowledge the molecular formulæ of solid bodies is provisional rather than absolute.

The molecular weights of gases have been already explained in connection with Avogadro's law; it may, however, be well to definitely place on record that **the molecular weight of any gas is the weight of that volume which occupies the same space as do two parts by weight of hydrogen.**

84. **Absolute weight of Hydrogen.**—Hydrogen being taken as the unit of density, its absolute weight is in many calculations a matter of much importance. As a result of most careful determinations it is found that **1 litre of hydrogen at the normal temperature and pressure weighs 0·0896 gram, or 11·2 litres weigh 1 gram.** From this the weight of any other gas of known composition is easily deduced. **The weight in grams of a litre of any gas is its density ×0·0896; and the number representing the density is identical with the weight in grams of 11·2 litres of the gas.**

85. **Chemical calculations.**—The laws governing the combination of substances by weight and volume being understood, most ordinary chemical calculations of percentages, quantities, &c., resolve themselves into arithmetic problems of the simplest nature. The readiest method of explaining these will be by the aid of a few examples.

86. **Formula from percentage composition.**—Analytic results are usually expressed in percentages, and one of the first calculations necessary is that required in order to deduce its simplest formula—in other words, its atomic composition Let us take the following as an example. A

body has the following percentage composition; required its formula:—

Magnesium	3·98
Calcium	13·28
Potassium	12·99
Sulphuric acid (SO_4) . . .	63·77
Water (H_2O)	5·98
	100·00

On dividing each of the numbers representing the percentage of the element present by its atomic weight, a series of numbers is obtained which are in the ratio of the number of atoms present of each element:—

$$\frac{3·98}{23·94} = 0·166 \text{ of Mg.}$$

$$\frac{13·28}{39·9} = 0·332 \text{ of Ca.}$$

$$\frac{12·99}{39·04} = 0·332 \text{ of K.}$$

$$\frac{63·77}{95·82} = 0·665 \text{ of } SO_4.$$

$$\frac{5·98}{17·96} = 0·332 \text{ of } H_2O.$$

The weights taken for the groups sulphuric acid, SO_4, and water, H_2O, are the sums of those of the atoms present. An inspection of these numbers shows that they bear a very simple relationship to each other. On dividing each of the series by the lowest number we have

$$\frac{0·166}{0·166} = 1 \text{ of Mg.} \quad \frac{0·332}{0·166} = 2 \text{ of Ca.} \quad \frac{0·332}{0·166} = 2 \text{ of K.}$$

$$\frac{0·665}{0·166} = 4 \text{ of } SO_4 \quad \frac{0·332}{0·166} = 2 \text{ of } H_4$$

From these results the simplest possible formula becomes $MgCa_2K_2(SO_4),2H_2O$.

At times the result of such calculation will not work out in whole numbers; thus in deducing the formula of nitrogen

pentoxide from its percentage composition the result obtained is

1 of nitrogen to 2·5 of oxygen.

As from the definition fractions of an atom are impossibilities, this result must be doubled, and the obvious formula is N_2O_5. In all cases where the calculated formula contains the fraction of an atom, the simplest multiple must be taken which converts this fraction into a whole number.

87. Percentage composition from formula.—At times this reverse operation to that just described has to be performed. Thus felspar has the formula KAl,Si_3O_8 ; required its percentage composition. The weight of the molecule from the formula is

K	.	.	.	.	39·04
Al	.	.	.	.	27·30
Si_3	28·0	×	3	=	84·00
O_8	15·96	×	8	=	127·68
Molecular weight .				.	278·02

From this it follows that 278·02 parts of felspar contain 39·04 parts of potassium, and the number of parts in 100 is required. A series of ordinary calculations in simple proportion give the percentage composition:—

As 278·02	100 ::	39·04	:	14·04	per	cent.	of	K.
„ 278·02	100 ::	27·30	:	9·82	„	„	„	Al.
„ 278·02	100 ::	84·00	:	30·21	„	„	„	Si.
„ 278·02	100 ::	127·68	:	45·92	„	„	„	O.
				99·99				

88. Calculation of Quantities.—To determine the quantities participating in any chemical change it is necessary first of all to be sufficiently familiar with the change itself to express the reaction by means of a chemical equation. All else is then perfectly simple. The following problem may be taken as an example :—

What weight in kilograms of zinc and sulphuric acid will yield hydrogen enough to fill a balloon of 350 cubic mètres

capacity at 15° C. and 735^{mm} pressure; and what fraction of the gas will escape when the balloon has reached an elevation where the barometer stands at 335^{mm}, supposing first the temperature to have remained constant, and secondly to have dropped to 5° C.?

The first step necessary is to find the weight of hydrogen required to fill the balloon, and to do this the volume must be reduced to normal temperature and pressure, which is done in the following manner:—

$$\frac{350 \times 273 \times 735}{288 \times 760} = 320{\cdot}8 \text{ cubic mètres.}$$

(This equation simply embodies the law that the volume is directly as the absolute temperature, and inversely as the pressure.)

The mètre being ten decimètres, the cubic mètre has a capacity of 1,000 litres, consequently 11·2 cubic mètres of hydrogen at N.T.P. weigh 11·2 kilograms; and

$$\frac{320{\cdot}8}{11{\cdot}2} = 28{\cdot}6 \text{ kilograms of hydrogen required.}$$

According to the equation,

$$\underbrace{\underset{2}{H_2} + \underset{31{\cdot}98}{S} + \underset{63{\cdot}84}{O_4}}_{97{\cdot}82} + \underset{64{\cdot}9}{Zn} = \underbrace{\underset{64{\cdot}9}{Zn} + \underset{31{\cdot}98}{S} + \underset{63{\cdot}84}{O_4}}_{160{\cdot}72} + \underset{2.}{H_2}$$

That is to say, 97·82 parts of sulphuric acid, and 64·9 of zinc yield 2 parts by weight of hydrogen; these quantities being the molecular weights of the bodies participating in the change. Then,

As 2 : 28·6 :: 97·82 : 1398·8 kilograms of sulphuric acid required;

As 2 : 28·6 :: 64·9 : 928 kilograms of zinc required.

We next have to deal with the fraction which has escaped; in the first place, the gas will have expanded inversely as the pressure,—

$$\frac{350 \times 735}{335} = 76. \qquad \text{at 335 mm.}$$

Of these $767-350=417$ mètres, or $\frac{417}{767}$ of the original quantity of gas must have escaped.

The expansion in the second case is found thus :—

$$\frac{350 \times 735 \times 278}{335 \times 288} = 749 \text{ mètres at } 335^{mm}, \textit{ and } 5° \textit{ C.}$$

Of these $749-350 = 399$ mètres, or $\frac{399}{749}$ of the original quantity of gas must have escaped.

The above represents a particularly involved calculation of quantities. Again, let it be repeated that it is first necessary to know the chemical equation representing the change that occurs. Then the relative weights of each substance participating therein may be obtained from the atomic weights, and the relation between volume and weight of gases from their densities. If the foregoing explanations have been clearly grasped, there should be no difficulty in making any of the quantity calculations arising from ordinary chemical work.

89. **Gaseous volumes.**—The following is a slightly different type of calculations, in which gaseous volumes are involved.

What volume of carbon dioxide must be passed over red-hot charcoal to yield 159 litres of carbon monoxide?

First giving the equation by which the action is represented,—

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Carbon.}}{C} = \underset{\text{Carbon monoxide.}}{2CO.}$$

In this reaction, one molecule of carbon dioxide is converted into two molecules of carbon monoxide; and as the gaseous volume is in direct proportion to the number of molecules, one volume of carbon dioxide yields two volumes of the monoxide; and

as 2 : 1 :: 159 : 79·5 litres of carbon dioxide required.

90. **Atomic weight calculations.**—The following is an instance of calculations of this type.

Pure carbon monoxide is passed over red-hot copper oxide; the residual metal and the carbon dioxide formed are weighed;

in one experiment 24·360 grams of oxygen were lost and 67·003 grams of carbon dioxide were obtained. From this calculate the atomic weight of carbon (O=15·96).

Assuming that by other means it has been ascertained that the chemical change referred to is represented by the following equation,

$$\underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Copper oxide.}}{CuO} = \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Copper.}}{Cu}$$

then it is evident that

$$\underset{\text{Wt. of } CO_2.}{67{\cdot}003} - \underset{\text{Wt. of O.}}{24{\cdot}360} = \underset{\text{Wt. of CO.}}{42{\cdot}643}$$

and as CO_2 contains double as much oxygen as CO, then

$$\underset{\text{Wt. of CO.}}{42{\cdot}643} - \underset{\text{Wt. of O.}}{24{\cdot}360} = \underset{\text{Wt. of C.}}{18{\cdot}283}$$

Therefore carbon monoxide consists of 24·360 of oxygen to 18·283 of carbon; and as it is also assumed that it contains an atom of each element, and that the atomic weight of oxygen is 15·96, then

as 24·360 : 15·96 :: 18·283 : 11·98=atomic weight of carbon.

91. Calculations based on Gaseous diffusion.—As an example of calculations of this type, the following is appended:—

How can the density of a gas be determined from its rate of diffusion? If a gas diffuses 1·0143 times as rapidly as air, what is its density?

The rate of gaseous diffusion being inversely as the square root of the density, the density must of necessity be inversely as the square of the rate of diffusion. In terms of hydrogen the density of air is 14·47, and therefore

as $1{\cdot}0143^2 : 1^2 :: 14{\cdot}47 : 14{\cdot}04$=density of gas in question.

CHAPTER VII

NOMENCLATURE; ACIDS AND ALKALIES, ETC.

92. Names of Metals.—The names given to the elements are, as a rule, in no way connected with their properties: the only attempt at system is that the termination *um* is restricted to the metals. Selenium and tellurium, however, are exceptions, as, when discovered, they were supposed to be metallic elements. It has been proposed to change the names to selenion and tellurion; this has not, however, met with general acceptance.

93. Binary Compounds.—Bodies which contain only two elements are called *binary compounds*. Their names are fixed by rule; but in the case of the more well-known compounds, the old or 'trivial' names are almost always used; no one would think, for example, of calling water hydrogen monoxide. The name of a body should, as far as possible, indicate its composition; this end is attained by making the name of a binary compound consist of derivatives of the names of the two elements. There are unfortunately several modifications of each name, different chemists using different methods of nomenclature. The student must make himself familiar with the whole, as, in the course of reading, he is sure to meet with the same body under names different from one another. Very little practice is, however, sufficient to overcome this difficulty.

The most frequently occurring binary compounds are those composed of a metal and non-metal; the name of the metal is first written, and one or more syllables being removed the termination *ide* is added to the name of the non-metal. The compound of copper and oxygen is thus called *copper oxide*; that of copper and sulphur, *copper sulphide*, and so on for other compounds. These names are sometimes written *oxide of copper* and *sulphide of copper* respectively. Another plan consists of changing the Latin name of the metal into an adjective

by substituting *ic* for its last syllable; the above names thus become *cupric oxide* and *sulphide.*

We frequently find that more than one compound of the same elements is known; it then becomes necessary to use names which shall discriminate the one from the other. Oxygen and copper combine in two different proportions, represented by the formulæ CuO and Cu_2O; the name oxide is common to both, but the second is called cupr*ous* oxide. The termination *ous* is applied to the compound containing the lower proportion of oxygen or other non-metallic element. Where there are two or more atoms of the metalloid present in a compound, the distinction is marked by the use of a prefix to the second name indicating the number. The two oxides of barium, BaO and BaO_2, are thus known respectively as barium monoxide and dioxide. Occasionally the prefixes *proto* and *per* are attached to the second name; *proto* to the compound in which the lower proportion of the non-metallic element occurs, *per* to that containing the higher: barium monoxide and dioxide become barium protoxide and peroxide. There is one series of oxides in which there are two atoms of the metal to three of oxygen, as Fe_2O_3; these are sometimes termed sesquioxides: the name is, however, dying out. Where there are several binary compounds of the same elements, or where the molecule is a complex one, the number of atoms of each element is indicated by a prefix thus, triferric tetroxide, Fe_3O_4. In binary compounds among the non-metals, the termination *ide* is usually given in preference to oxygen, chlorine, and sulphur; thus we have carbon oxides and sulphides, phosphorus chlorides, and chlorine oxides.

94. Ternary and Higher Compounds.—The name 'ternary' is applied to those compounds containing three elements. Among the compounds higher than the binary series are those formed by the union of water with oxides, thus forming acids, and hydrates (hydroxides), and derivatives of these bodies.

The oxides soluble in water have already been classified into those capable of turning a solution of litmus red, and

others which possess the property of restoring to the reddened solution its blue colour. Based on this reaction is a division of the various oxides into two important classes, to which attention must now be directed.

95. **Acids.**—The name acid is a familiar one, because it is continually applied in every-day parlance to everything which is sour. A number of bodies possess this distinction in common; to the chemist the sourness of an acid is but an accidental property, as, according to his definition of these bodies, substances are included as acids that are not sour to the taste. **An acid may be defined as a body containing hydrogen, which hydrogen may be replaced by a metal (or group of elements equivalent to a metal) when presented to it in the form of an oxide or hydrate (hydroxide).**

As a class, the acids are sour; they are also active chemical agents. Most acids are characterised by the property of changing the colour of a solution of litmus, a naturally blue body, to a red tint. This, as the student has just been reminded, is one of the properties of the solution of certain oxides in water. In these instances chemical union occurs between the oxide and water, resulting in the production of an acid as a distinct chemical compound; thus the addition of water to sulphur trioxide produces sulphuric acid:—

$$\underset{\text{Sulphur trioxide.}}{SO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric acid.}}{H_2SO_4}$$

Oxygen is a constituent of most acids, the members of this group being distinguished as 'oxy-acids.' The oxides, which by union with water form acids, are termed anhydrides, or anhydrous acids. They are in most cases non-metallic oxides, but sometimes consist of metals combined with a comparatively large number of atoms of oxygen. There are a few acids in which oxygen is absent: these are termed 'hydr-acids': hydrochloric acid, HCl, is an example of this class. According to the definition given (which is accepted by the great majority of chemists), hydrogen is an essential constituent of all acids. It should, however, be mentioned that some chemists apply

the term acid to what are here termed anhydrides; consequently CO_2 (carbon dioxide, or carbonic anhydride) is sometimes described as carbonic acid gas. This name is now, however, being replaced by that more in accordance with the theories of modern chemical science.

96. **Bases and Alkalies.**—The oxides which, when dissolved in water, restore the blue colour to reddened litmus are called alkalies: they form a subdivision of a larger class of oxides, the whole of which combine readily with acids, and are known as bases.

A base is a compound, usually an oxide, or hydrate, of a metal (or group of elements equivalent to a metal), which metal (or group of elements) is capable of replacing the hydrogen of an acid when the two are placed in contact. The greater number of metallic oxides are bases. Bases, as well as acids, differ considerably in their chemical activity. As already mentioned, certain bases which dissolve in water are termed alkalies.

An alkali is a base of a specially active character, soluble in water, to which it imparts a soapy taste and touch. Alkalies restore the blue colour to reddened litmus. The principal alkalies are sodium hydrate, $NaHO$, and potassium hydrate, KHO. A solution of ammonia gas in water is also alkaline, and is often termed ammonium hydrate.

Paper tinted yellow with turmeric is also used as a test for alkalies, which give the paper a reddish-brown hue.

The hydrates are mostly compounds of metallic oxides with water; they are sometimes termed hydroxides, or hydrated oxides. Their formation is represented by the following equations:—

$$\underset{\text{Sodium oxide.}}{Na_2O} + H_2O = \underset{\text{Sodium hydrate.}}{2NaHO.}$$

$$\underset{\text{Calcium oxide.}}{CaO} + H_2O = \underset{\text{Calcium hydrate.}}{CaH_2O_2.}$$

97. **Salts.—When an acid and base react on each other, the body produced by the replacement of the hydrogen of the acid by the metal of the base is termed a salt.** Water is also formed during the reaction. The

action of the stronger acids and bases on each other is very violent; the resultant salts are usually without action on litmus. This is, however, not always the case; for when a strong acid combines with a weak base, the salt is acid to litmus: nitrate of mercury is an example. When the base is a strong one and the acid weak, as in sodium carbonate, the salt has an alkaline reaction. Litmus is itself a salt of a vegetable acid and base possessing a blue colour. An acid, when added, displaces the weak vegetable one, and forms a salt with the base; the litmus acid, being red, gives the solution a red tint. On adding a base it combines with the acid; the litmus acid and base being liberated again unite, with the restoration of the blue colour. The following are instances of the formation of salts by the union of acids and bases:—

HCl	+	$NaHO$	=	$NaCl$	+	H_2O.
Hydrochloric acid.		Sodium hydrate.		Sodium chloride.		Water.
H_2SO_4	+	CaO	=	$CaSO_4$	+	H_2O.
Sulphuric acid.		Calcium oxide (quicklime).		Calcium sulphate.		Water.
HCl	+	NH_4HO	=	NH_4Cl	+	H_2O.
Hydrochloric acid.		Ammonium hydrate.		Ammonium chloride.		Water.

The acids are sometimes termed salts of hydrogen; thus sulphuric acid would be called hydrogen sulphate.

98. Names of Acids and Salts.—The names of acids are derived from those of their principal constituents by changing them into adjectives ending in *ic*; thus from sulphur we have sulphuric acid, and from nitrogen, nitric acid. The hydracids are distinguished by the prefix *hydro*, as hydrochloric acid. The names of the corresponding salts are derived from the same root by adding *ate*; the salts of sulphuric and nitric acids are respectively sulphates and nitrates.

When an element forms two oxides, both of which unite with water to form acids, the acid containing the higher proportion of oxygen receives the name ending in *ic*; for the other the termination *ous* is substituted. There are, for instance, two oxides of sulphur, SO_2 and SO_3: these are termed—

SO_2 Sulphurous anhydride. SO_3 Sulphuric anhydride.

Both combine with water, becoming—

SO_2	+	H_2O	=	H_2SO_3.
Sulphurous anhydride.		Water.		Sulphurous acid.
SO_3	+	H_2O	=	H_2SO_4.
Sulphuric anhydride.		Water.		Sulphuric acid.

The salts of an acid whose name ends in *ous* have the termination *ite* :—

H_2SO_3	+	$2NaHO$	=	Na_2SO_3	+	$2H_2O$.
Sulphurous acid.				Sodium sulphite.		

In describing the basic component of a salt, the simplest method is to mention the name, as potassium sulphate. At times it is convenient to change this into the adjective form. When this is done, the same termination is used as is applied to the base itself; thus, salts formed by the action of mercuric oxide (HgO) on acids are called mercuric salts; those from mercurous oxide (Hg_2O), mercurous salts :—

HgO	+	$2HCl$	=	$HgCl_2$	+	H_2O.
Mercuric oxide.		Hydrochloric acid.		Mercuric chloride.		
Hg_2O	+	$2HCl$	=	Hg_2Cl_2	+	H_2O.
Mercurous oxide.		Hydrochloric acid.		Mercurous chloride.		

The salts of the hydracids, being binary compounds, have names ending in *ide*.

CHAPTER VIII

QUANTIVALENCE AND BASICITY

99. **Quantivalence.**—Remembering that the only absolute method of determining the molecular constitution of bodies is by an investigation of their densities in the gaseous state, the following table is exceedingly instructive—

Column No. I. gives the name.
„ II. The formula corresponding to the observed density.
„ III. The molecular weight as deduced from the formula; that is, the sum of all the atomic weights.
„ IV. The density as calculated from the molecular weight, being $\frac{1}{2}$ mol. wt.
„ V. The density as determined experimentally.

I. Name	II. Formula	III. Molecular Weight	IV. Calcd. Density	V. Observed Density
I.				
Hydrofluoric acid	HF	20·1	10·05	—
Hydrochloric acid	HCl	36·37	18·18	17·99
Hydrobromic acid	HBr	80·76	40·38	39·10
Hydriodic acid	HI	127·53	63·76	64·07
Iodine monochloride	ICl	161·9	80·95	—
Mercurous chloride	$HgCl$	235·2	117·6	120·49
Mercurous bromide	$HgBr$	279·6	139·8	146·31
II.				
Water	OH_2	17·96	8·98	8·98
Sulphuretted hydrogen	SH_2	33·98	16·99	17·18
Cadmium bromide	$CdBr_2$	271·1	135·55	133·67
Lead chloride	$PbCl_2$	277·1	138·55	137·08
Mercuric chloride	$HgCl_2$	270·5	135·25	141·41
Mercuric bromide	$HgBr_2$	359·3	179·65	175·47
Mercuric iodide	HgI_2	452·9	226·45	233·76
III.				
Boron fluoride	BF_3	68·1	34·05	33·33
Boron chloride	BCl_3	117·0	58·5	58·00
Boron bromide	BBr_3	250·2	125·1	126·69
Ammonia	NH_3	17·01	8·5	8·61
Phosphine	PH_3	33·96	16·98	17·03
Phosphorous chloride	PCl_3	137·07	68·53	70·42
Arseniuretted hydrogen	AsH_3	77·9	38·95	38·81
Arsenious chloride	$AsCl_3$	181·0	90·5	91·91
Arsenious iodide	AsI_3	454·5	227·25	232·32
Antimony chloride	$SbCl_3$	225·7	112·85	112·55
Bismuth chloride	$BiCl_3$	313·6	156·8	163·78
IV.				
Marsh gas	CH_4	15·97	7·98	8·03
Carbon tetrachloride	CCl_4	153·45	76·72	76·91
Silicon fluoride	SiF_4	104·4	52·2	51·51
Silicon chloride	$SiCl_4$	169·5	84·75	85·71
Silicon iodide	SiI_4	534·1	267·05	275·61
Vanadium chloride	VCl_4	192·7	96·35	96·53
Stannic chloride	$SnCl_4$	258·9	129·45	132·95
V.				
Phosphorus fluoride	PF_5	126·3	63·15	—
Molybdenum chloride	$MoCl_5$	272·4	136·2	136·51
Tungsten pentachloride	$WoCl_5$	360·9	180·45	183·26
VI.				
Tungsten hexachloride	$WoCl_6$	396·2	198·1	190·47

An inspection of this table shows that first we have a group of molecules containing one atom only of each element, and representing therefore the simplest compounds possible. The elements, H, F, Cl, Br, and I are distinguished by this property of having their combining power in the gaseous molecule exhausted as soon as one of their atoms has combined with one atom of any other element. In the second class we have a series of elements, whose single atoms combine with two atoms of members of the first group. In the third group we have elements combining with three such atoms, while in the fourth, fifth, and sixth, they combine respectively with four, five, and six first group atoms. The elements studied in the preceding table, at least, have different values of atom-combining power. **The measure of the number of atoms of other elements, with which one atom of each element can combine, is termed Quantivalence, or Atomicity.**

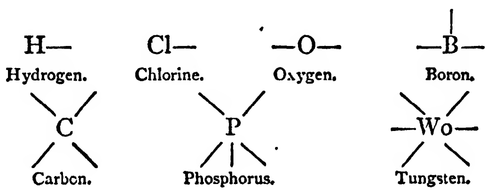
The quantivalence of each member of the first group is *one* in the particular compounds there given, and hence such elements are styled 'monovalent or monads.' The following nomenclature has been proposed to distinguish the various groups :—

Group	I.	Monovalent	or	Monads.
„	II.	Divalent	„	Dyads.
„	III.	Trivalent	„	Triads.
„	IV.	Tetravalent	„	Tetrads.
„	V.	Pentavalent	„	Pentads.
„	VI.	Hexavalent	„	Hexads.

Examination of such a series of compounds as that we have been studying shows that a definite relation exists between the quantivalence of an element and its chemical equivalent and atomic weight. **The quantivalence of an atom represents the number of times the equivalent weight of the element is contained in its atomic weight.** Thus the atomic weight and equivalent of oxygen are respectively 15·96 and 7·98 ; and

$$\frac{15·96}{7·98} = 2, \text{ which is the quantivalence of oxygen.}$$

100. Graphic Notation.—The exact nature of the force by which the atoms of elements are bound together to form a compound is unknown to us; but we see that we can attach a numerical value to such connecting or linking power of each atom. Thus the atom of hydrogen has its combining capacity exhausted when it has united with one atom of another element: tungsten, on the other hand, does not suffer similar exhaustion until united directly with six atoms of some other element. This linking power is expressed graphically by attaching to the symbol of the element a number of lines each representing one link or unit of valency (atom-combining power). The following are examples of such graphic symbols:—

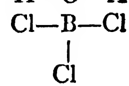


Adopting this system of notation it is an easy step forward to represent compounds by what are termed graphic formulæ, that is, formulæ in which the valency of each atom is shown by these graphic representations of lines, and the probable mode of linking in the various compounds by the disposition of these lines between the atoms. Thus we have the following examples of graphic formulæ:—

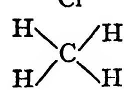
Hydrochloric acid, H—Cl

Water, H—O—H

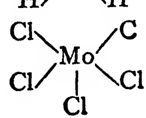
Boron chloride,

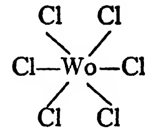


Carbon hydride (marsh gas),

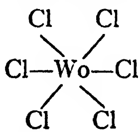


Molybdenum chloride,

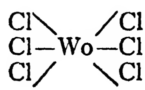


Tungsten hexachloride, 

Graphic formulæ are explained at this stage because of the assistance they will render in the following paragraphs. One word of caution is perhaps necessary: the lines in graphic formulæ are only intended to indicate the number and disposition of the valencies of each atom. They must not be viewed as any representation of the actual position physically of the atoms in regard to each other. Thus tungsten chloride may be represented by either



or



The position and length of the links is merely a matter of convenience at the time of writing the formula.

101. Variable Quantivalence.— Examination of the table in the last but one paragraph shows that different elements appear in more than one class; thus mercury forms two chlorides and bromides, being a monad in the one series and a dyad in the other. Tungsten also forms two distinct chlorides, in which it is pentavalent and hexavalent respectively. We therefore see that the number of atoms of other elements with which the atom of one element combines is not absolutely constant. The question arises whether in such different compounds the actual valency or quantivalence of the element has changed, or that the valency is in the one case unsatisfied. Thus, taking the two mercury chlorides, must the graphic formulæ be written—

$$\mathrm{Hg{-}Cl} \text{ and } \mathrm{Cl{-}Hg{-}Cl}$$

or

$$\mathrm{{-}Hg{-}Cl} \text{ and } \mathrm{Cl{-}Hg{-}Cl}\,?$$

As a result of investigations of such series of compounds, abundant evidence has been accumulated which shows that in

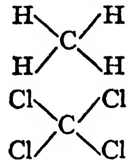
cases where an element has different valencies in different compounds, in the lower members of such series an unsatisfied valency exists. This is exhibited by the ease with which the compound assimilates additional atoms by which its normal or higher valency is fully engaged. **It is perfectly competent for an element to form a compound in which a portion of its valency remains unsatisfied, but such compounds usually combine readily with additional atoms.**

An inspection of our table, page 125, shows that the valency of an element is usually the same by whichever of the monad elements it may be measured. For example, whether H,Cl, or Br be taken as the unit, we find that combination is with the same number of atoms of each; thus we have, BF_3 and BCl_3; PH_3 and PCl_3; CH_4, and CCl_4.

The next question is whether elements exhibit the same valency towards a dyad as a monad element; thus should the divalency of an oxygen atom be equally satisfied with the divalency of another dyad atom, as it is with the valencies of two monad atoms? Before answering this question it will be well to give a table of such compounds, containing polyvalent atoms, as have had their molecular weight satisfactorily determined.

I. Name	II. Formula	III. Molecular Weight	IV. Calcd. Density	V. Observed Density
I.				
Carbon monoxide . . .	CO	27·93	13·96	13·96
Nitric oxide	NO	29·97	14·98	15·00
II.				
Nitrogen peroxide. . .	NO_2	45·93	22·96	22·94
Nitrous oxide . . .	ON_2	43·98	21·99	21·93
Sulphur dioxide . . .	SO_2	63·90	31·95	32·46
Selenium dioxide . . .	SeO_2	109·9	54·95	58·15
Carbon dioxide . . .	CO_2	43·89	21·94	22·07
Carbon disulphide . .	CS_2	75·93	37·96	38·09
III.				
Sulphur trioxide . . .	SO_3	79·86	39·93	43·43
IV.				
Osmic anhydride . . .	OsO_4	262·4	131·2	128·42

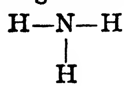
Examining this table we find that carbon combines with two atoms of oxygen and of sulphur as against four of hydrogen or chlorine, a fact expressed in the following graphic formulæ:



$O{=}C{=}O.$

$S{=}C{=}S.$

So far it would seem that the tetravalent atom of carbon has its valencies equally satisfied with either four atoms of a monad or two of a dyad; but there is not the same uniformity throughout, three gaseous compounds of nitrogen with oxygen are given and in no case does the valency agree with that of nitrogen in its compound with hydrogen, NH_3 (ammonia). Indicating the valencies by graphic formulæ we have



$—N{=}O \qquad —O—N{=}O \qquad {=}N—O—N{=}$

In each of the three cases, there are unsatisfied links, and in that of NO_2, in which nitrogen figures as a triad, there is one oxygen link unmentioned. According to its hydrogen valency, nitrogen should combine with oxygen in the proportion of one atom of nitrogen to one and a half of oxygen (in whole numbers, 2 to 3), whereas in this particular compound the proportion is one to two.

Apart from irregularities of the kind just described, examination shows that a number of elements have greater relative combining powers with oxygen than with hydrogen or the monads. Thus nitrogen combines with three atoms of hydrogen, and with two atoms of oxygen. Sulphur and selenium each combine with two atoms of hydrogen, forming respectively SH_2 and SeH_2: but with oxygen they produce the following compounds, in which sulphur and selenium must be represented as possessing a much higher valency—sulphur dioxide, SO_2; sulphur trioxide, SO_3; and selenium dioxide, SeO_2. Further investigation would show that several other

elements have a higher relative combining power with oxygen than with the monad hydrogen.

In the compounds of the positive elements, hydrogen and the metals, with such strongly negative elements as the chlorine and sulphur groups, there is not a single example of chlorine, bromine, or iodine acting otherwise than as monad elements, while sulphur, selenium, and tellurium are throughout divalent. On the other hand, chlorine, bromine, and iodine are polyvalent, and probably heptavalent to negative elements such as oxygen. Further, as in the compounds previously cited, sulphur and selenium are hexavalent to oxygen.

This second table affords further examples of compounds which possess unsatisfied atom-combining power, and which enter very readily into combination with other atoms. Very striking among these is carbon monoxide, which not only readily combines with oxygen, but also with chlorine and other bodies :

Carbon monoxide.	Carbon dioxide.	Phosgene gas.
$=C=O$	$O=C=O$	$\begin{matrix} Cl \diagdown \\ \quad C=O \\ Cl \diagup \end{matrix}$

102. Quantivalence in Solid Molecules.—There is considerable difficulty in determining the quantivalence of elements from their solid compounds, because we have at present no certain knowledge of the constitution of such molecules. There are compounds which form gaseous and solid allotropic modifications, due probably entirely to the greater molecular weight in the solid form. Thus in the preparation of cyanogen gas, C_2N_2. a brown powder is formed, having the same percentage composition as cyanogen. This brown powder, paracyanogen, is capable of being volatilised when heated in a current of carbon dioxide or nitrogen ; and is thus converted into cyanogen gas, by a chemical change which may thus be represented :—

$$\underset{\text{Paracyanogen.}}{C_x N_x} \quad = \quad \underset{\text{Cyanogen.}}{\frac{x}{2}\, C_2 N_2}$$

In other words the complex solid molecule splits up into a number of simpler gaseous molecules. This is not merely an

isolated instance, for abundant evidence exists to show that the molecules of gaseous bodies are frequently different in composition to those of the same compounds in the liquid or solid state. - But, so far as we know, the molecular weight of a compound when solid may be more, but it is never less than is the weight of a gaseous molecule of the same body.

In ascribing molecular formulæ to solid bodies, it is customary to assume that when atoms of different elements replace each other, the type of the formula remains constant whether the body be gaseous or solid. This is convenient, but it must be remembered that the custom is in many instances purely arbitrary and has no actual experimental foundation. To make this clear by example, we know HCl to be the formula of hydrochloric acid, and that an atom of sodium and other metals replaces the hydrogen in primary chlorides; it is assumed that these chlorides have the same typical formulæ—

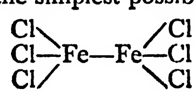
H—Cl   Na—Cl   K—Cl   Ag—Cl &c.

These elements—sodium, potassium, and silver—are consequently assumed to be monads.

In the same way other elements, as zinc, barium, &c., combine with two atoms of chlorine and form chlorides, to which the following formulæ have been assigned :—

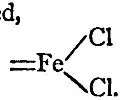
Cl—Zn—Cl   Cl—Ba—Cl.

Iron and copper are examples of bodies which form more than one chloride. Thus of iron we have the chlorides represented by the two formulæ $FeCl_2$ and $FeCl_3$ while the copper chlorides are CuCl and $CuCl_2$. These are the simplest possible formulæ in each case, and would lead us to assume that for chlorine iron has a maximum valency of III. But ferric chloride (the higher of the two) is one of those compounds which has had its density determined in the gaseous state, and this simplest possible formula requires to be doubled. Accordingly the molecule of ferric chloride is represented by Fe_2Cl_6. As the two iron atoms must be united by at least one link of valency, we have, as the simplest possible graphic formula,

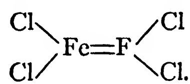


in which iron is assumed to be a tetrad. Throughout the whole group of ferric compounds it is assumed that the molecule contains two iron atoms linked together, and having between them a total valency of VI.

Our attention must next be turned to the lower chloride, represented by the simplest formula $FeCl_2$. Now unless there is decisive evidence to the contrary, it is fair to assume that a compound does not contain unsaturated valencies, and $Fe Cl_2$ shows two links unsatisfied,



If the formula be doubled, we have Fe_2Cl_4, and the graphic formula,



in which the tetravalence of iron is satisfied. Again if $FeCl_2$ be taken as the formula of the lower chloride, we have the amalgamation of two of the simpler molecules with two additional atoms of chlorine to form the higher chloride thus,

$$\underset{\text{Ferrous chloride.}}{2FeCl_2} \quad + \quad \underset{\text{Chlorine.}}{Cl_2} \quad = \quad \underset{\text{Ferric chloride.}}{Fe_2Cl_6}.$$

This is unlikely because the higher body is the more stable, and usually of compounds of the same elements those are more stable which contain the least number of atoms. It is more likely that ferrous chloride is represented by even higher multiples of $FeCl_2$, as Fe_3Cl_6 or Fe_4Cl_8. Notwithstanding this, ferrous chloride is almost invariably written $FeCl_2$; **it must be remembered that for the great majority of solid compounds, the formulæ commonly employed are not necessarily true molecular formulæ.**

The copper chlorides are generally represented by the formulæ Cu_2Cl_2 and $CuCl_2$,

$$Cl—Cu—Cu—Cl \text{ and } Cl—Cu—Cl,$$

in this case the probability is greater that the formulæ correctly represent the molecules.

It will be seen that the valency of elements which only

form solid compounds is difficult to determine, because, as has been insisted on, of the uncertainty of the actual molecular constitution of such compounds; but in the table given on page 129 the probable maximum valency of the elements has been inserted. It must, however, be remembered that these numbers are not in every case capable of direct verification; neither do they of necessity represent the valency of the elements in all their compounds.

103. Odd and even Valencies.—Examination of a number of series of compounds shows that in many instances the active valency of an element increases or diminishes by two. Thus we have carbon monoxide, CO, and carbon dioxide, CO_2; phosphorus chloride, PCl_3, and phosphorus fluoride, PF_5. Making use of graphic formulæ, the free or unsaturated valencies of the lower compounds of these two pairs are represented by

$$=\mathrm{C}=\mathrm{O} \qquad \text{and} \qquad =\mathrm{P}\begin{matrix}\diagup \mathrm{Cl} \\ -\mathrm{Cl} \\ \diagdown \mathrm{Cl}\end{matrix}$$

It has been assumed that in such cases the units of valency combine with each other in pairs, and so become latent. Under this hypothesis the active valency of an element must be represented by either an even or an odd number, and accordingly the elements have been divided into *perissads* whose valency is odd, and those having even valencies, which are termed *artiads*. This classification has, however, dropped into disuse, because in the first place the number of free valencies in unsaturated compounds is not always represented by an even number (tungsten, for instance, is both perissad and artiad in its chlorides); secondly, there is not sufficient proof that such union between the valency links does take place. The frequency with which active valency increases or diminishes by two may be partly accounted for by the fact that oxygen and some other of the most commonly occurring elements are dyads. Whenever a single atom of an element forms two or more oxides the valency must increase or diminish by two; thus we have barium oxide and peroxide, lead oxide and peroxide, and sulphur

dioxide and trioxide, all of which are examples of the case in point.

Ba=O	and	O=Ba=O
Pb=O	„	O=Pb=O
O=S=O	„	O=S(=O)=O

The above graphic formulæ show the increase in valency in each of the pairs of compounds.

The importance of the doctrine of quantivalence has led to its having been here somewhat fully treated; and in order that a proper estimate be gained of its position in theoretical chemistry, the student's attention has been also directed to its limitations and bounds. For this there is every necessity, in the face of Meyer's warning that the young generation is inclined to treat chemistry dogmatically, 'especially the doctrines of the chemical equivalence of the elements and the linking of atoms.'

104. **Basicity of Acids.**—In the formation of salts, the hydrogen of an acid is replaced by a metal. Hydrogen, being monovalent, is replaced by different metals in proportions varying according to their valency. The valency of the displacing metals must be equal to that of the total number of atoms of hydrogen displaced. Thus a monad metal will replace one atom of hydrogen; a dyad, two atoms, and so on. **The quantity of a base required to form a salt with an acid depends on the number of atoms of hydrogen present capable of replacement by the base; the measure of this quantity is termed the 'basicity' of the acid.** Those acids containing but one atom of replaceable hydrogen are termed monobasic, those with two and three such atoms are known respectively as dibasic and tribasic acids.

A monobasic acid requires one atom of a monad metal to form a salt, while with a dyad metal, two molecules of the acid are necessary. In every case such number of molecules of acid and atoms of metal must be taken as will give the same total valency of replaced hydrogen atoms as that of the replacing

metal. In the following table typical examples are given of the formation of salts :—

MONOBASIC ACID.

HNO_3	+	$NaHO$	=	$NaNO_3$	+	H_2O.
Nitric acid.		Sodium hydrate.		Sodium nitrate.		Water.
$2HNO_3$	+	CaH_2O_2	=	$Ca(NO_3)_2$	+	$2H_2O$.
		Calcium hydrate.		Calcium nitrate.		
$3HNO_3$	+	BiH_3O_3	=	$Bi(NO_3)_3$	+	$3H_2O$.
		Bismuth hydrate.		Bismuth nitrate.		

DIBASIC ACID.

H_2SO_4	+	$2NaHO$	=	Na_2SO_4	+	$2H_2O$.
Sulphuric acid.				Sodium sulphate.		
H_2SO_4	+	CaH_2O_2	=	$CaSO_4$	+	$2H_2O$.
				Calcium sulphate.		
$3H_2SO_4$	+	$2BiH_3O_3$	=	$Bi_2(SO_4)_3$	+	$6H_2O$.
				Bismuth sulphate.		

TRIBASIC ACID.

H_3PO_4	+	$3NaHO$	=	Na_3PO_4	+	$3H_2O$.
Phosphoric acid.				Sodium phosphate.		
$2H_3PO_4$	+	$3CaH_2O_2$	=	$Ca_3(PO_4)_2$	+	$6H_2O$.
				Calcium phosphate.		
H_3PO_4	+	BiH_3O_3	=	$BiPO_4$	+	$3H_2O$.
				Bismuth phosphate.		

105. Acid, Normal, and Basic Salts.—Salts such as those whose formulæ are given in the preceding table are termed normal salts. **A normal salt may be defined as that produced by the replacement of the hydrogen of the acid by its valency equivalent of a metal,** or group of elements functioning as a metal, in a base.

In the case of those acids which contain more than one atom of replaceable hydrogen, a portion only of such hydrogen is sometimes replaced; the result is a salt still possesing an acid character. **An 'acid' or 'hydric' salt is defined as that produced by the replacement of a portion only of the hydrogen of a polybasic acid by the metal of a base.** Acid sodium sulphate, $NaHSO_4$, is an example of a hydric or acid salt. An instructive group of compounds is

formed by the replacement of the hydrogen of phosphoric acid by sodium. In this way we have

Phosphoric acid . . .	H_3PO_4, acid reaction with litmus.
Dihydrogen sodium phosphate	H_2NaPO_4, acid reaction with litmus.
Hydrogen disodium phosphate	HNa_2PO_4, neutral reaction with litmus.
Sodium phosphate . .	Na_3PO_4, alkaline reaction with litmus.

Of the phosphates, the first two are hydric salts, while the third is normal. Formerly it was customary to term the normal salts, *neutral* salts; this phrase is inapplicable because, as in the examples before us, neutrality to litmus is not always associated with 'normal' constitution.

There are a few inorganic acids which contain non-replaceable hydrogen—for example, hypophosphorous acid, HPH_2O_2, and phosphorous acid, H_2PHO_3. In these cases the basic or replaceable hydrogen is placed at the commencement of the formula. The normal sodium hypophosphite is represented by the formula $NaPH_2O_2$. Care must be taken not to confuse salts of this type with those which are really acid salts.

There are certain oxy-acids which possess the power of combining with more of the base than is necessary to produce a normal salt. Sulphuric, nitric, and carbonic acids exhibit this property in a marked degree; especially in combination with certain bases, prominent among which are the oxides and hydrates of copper, lead, mercury, zinc, antimony, and bismuth. **A 'basic' salt is defined as that produced by the combination of an acid with a higher proportion of a base than is necessary for the formation of a normal salt.** The following are examples of basic salts; the additional quantity of base being distinguished by being placed outside a comma in the formula :—

Basic mercury sulphate (turpeth mineral)	$HgSO_4,(HgO)_2$.
Dibasic lead nitrate,	$Pb(NO_3)_2,PbH_2O_2$.
Green copper carbonate (malachite),	$CuCO_3,CuH_2O_2$.
Basic lead carbonate (white lead),	$(PbCO_3)_2,PbH_2O_2$

It will be noticed that in many of these basic salts the additional basic constituent is a metallic hydrate.

106. Molecular Constitution of Acids and Salts.—It is convenient to remember that every oxy-salt may be represented as a combination of the anhydrous acid and base. Thus we have the following :—

$$2NaNO_3 = Na_2O,N_2O_5.$$
$$Ca(NO_3)_2 = CaO,N_2O_5.$$
$$2Bi(NO_3)_3 = Bi_2O_3,(N_2O_5)_2.$$
$$Na_2SO_4 = Na_2O,SO_3.$$
$$CaSO_4 = CaO,SO_3.$$
$$2Na_3PO_4 = (Na_2O)_3,P_2O_5.$$
$$Ca_3(PO_4)_2 = (CaO)_3,P_2O_5.$$
$$2HNa_2PO_4 = H_2O,(Na_2O)_2,P_2O_5.$$
$$HgSO_4,(HgO)_2 = (HgO)_3,SO_3.$$
$$(PbCO_3)_2,PbH_2O_2 = (PbO)_2,PbH_2O_2,(Co_2)_2$$

In some cases this necessitates the doubling of the usual molecular formula, but as, in all probability, the true molecules of all such bodies are multiples of the ordinary formulæ, the double formula is within the true molecular constitution. The possibility of viewing the salts in this manner has led to a binary theory of their constitution in which it has been assumed, for instance, that the combination between Na_2O and N_2O_5 is analogous to that between Na and Cl to form sodium chloride. It is far more probable, however, that we must look upon a salt, as a whole, in which anhydride and base have no longer a separate individuality, rather than a binary compound of these two simpler compounds. Nevertheless, for the purpose of stating the composition of a body it is exceedingly convenient to give the proportion of each anhydride and base present. The results of analysis of mineral and other similar bodies are almost invariably so expressed, the percentage of each anhydride and base being given.

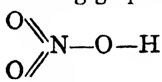
The problem of the constitution of acids has been attacked in another manner; taking, for example, sulphuric acid, it may be decomposed in various ways; thus an atom of chlorine may be made to replace an atom each of hydrogen and oxygen. The compound thus formed may have again the group HO re-

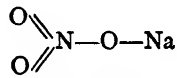
placed by another atom of chlorine, forming the body known as sulphuryl chloride. Below are the formulæ placed side by side :—

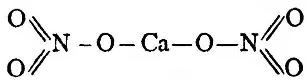
H_2SO_4,	$HClSO_3$,	Cl_2SO_2,
or $(HO)_2\ SO_2$	or $(HO)\ ClSO_2$	or Cl_2SO_2.
Sulphuric acid.	Sulphuryl chlorhydrate.	Sulphuryl chloride.

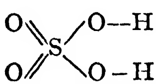
The displacement of HO is shown more clearly by writing the formulæ as shown in the second line.

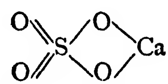
Investigations of this description lead to the conclusion that the replaceable hydrogen of an acid exists as a group or groups having the composition, HO, while the remaining oxygen is more directly and firmly combined with the sulphur or other dominant atom or atoms of the molecule. The probable constitution of some of the acids and their salts is indicated by the following graphic formulæ :—

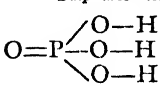

Nitric acid.

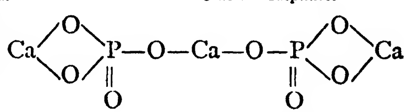

Sodium nitrate.


Calcium nitrate.

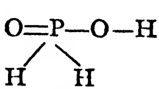

Sulphuric acid.

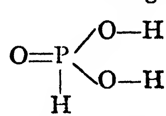

Calcium sulphate.


Phosphoric acid.

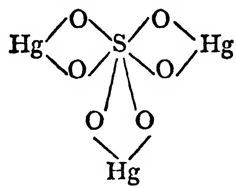

Calcium phosphate.

From these formulæ it will be seen that in the formation of the salts the hydrogen is simply replaced by the metal. Acids containing non-replaceable hydrogen have probably a constitution similar to that indicated by the following graphic formulæ, in which such hydrogen is connected direct to the grouping atom :—


Hypophosphorous acid.

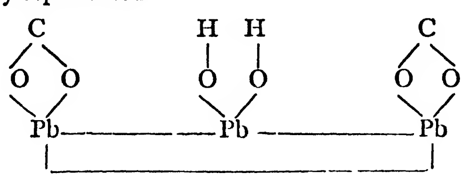

Phosphorous acid.

Little is known with certainty of the molecular constitution of basic salts. In some instances it would seem that the extra molecules of base replace the oxygen of the acid, as shown in the following formula for turpeth mineral—



This salt, it will be noticed, is identical with what would be the normal salt of a hexabasic sulphuric acid, having the formula H_6SO_6, *i.e.* ordinary sulphuric acid combined with two more molecules of water.

Other basic salts of which white lead may be taken as an example, are sometimes viewed as combinations of molecules of the normal salt with molecules of the additional base, in which case the actual linking must be extra-atomic. The existence of water of crystallisation is considered evidence of molecular combination, but extremely little is at present known of the nature of such combinations between molecules. It may also be assumed that in white lead we have a chemical compound in which the three atoms of lead are directly united together in the one molecule, in which case the constitution may be thus graphically represented—



It has been proposed to use, instead of ordinary formulæ, what are termed constitutional formulæ: these are simply formulæ so arranged as to indicate the probable constitution, or atomic arrangement, within the molecule. The following are illustrations of such formulæ of nitric and sulphuric acids respectively—NO_2HO, nitric acid; and $SO_2(HO)_2$, sulphuric acid.

Constitutional and graphic formulæ are frequently of considerable service to the chemist; but it must be remembered that they are not to be insisted on dogmatically. That white lead, for example, consists of some definite arrangement and linking of atoms cannot be doubted, and the graphic formula given above is useful as showing one view of such possible arrangement; but it does not necessarily follow that such an arrangement has been or is capable of actual proof. Graphic formulæ are simply intended as representing the hypothetic constitution of molecules, so far as our present knowledge enables us to speculate in that direction.

107. Acidimetry and Alkalimetry.—Among the various operations of quantitative analysis one most important series is that dealing with the estimation of the quantities of acid or alkali in various substances. The general principle adopted is that of adding, to a measured quantity of the substance, acid or alkali solution of known strength until the point of neutrality is reached. The test solutions are added from graduated measuring-vessels termed burettes, and the neutral point is determined by the use of some indicator, litmus being that most commonly employed.

For acidimetry and alkalimetry a series of standard solutions is prepared. These are commonly of the strength known by analysts as *normal* solutions. The normal acid solutions are prepared so that at 16° C. one litre shall contain 1 gram of the replaceable hydrogen of the acid. Consequently normal sulphuric acid solution must contain

$$\begin{array}{l} H_2 \quad S \quad O_4 \\ (2+32+64=98)\div 2 = 49 \text{ grams per litre} = 0{\cdot}049 \text{ gram} \\ \qquad\text{per c.c.} \end{array}$$

Similarly normal hydrochloric acid must contain

$$\begin{array}{l} H \quad Cl \\ 1+35{\cdot}37=36{\cdot}37 \text{ grams per litre} = 0{\cdot}036 \text{ gram per c.c.} \end{array}$$

The normal alkali solutions must contain per litre the chemical equivalent, weighed in grams of the hydrogen-replacing metal or group of elements. Thus normal sodium hydrate solution must contain

Na H O

$23 + 1 + 16 = 40$ grams per litre $= 0.040$ gram per c.c.

(Sodium and hydrogen are equivalent to each other, atom for atom.)

Normal barium hydrate (BaH_2O_2) solution must contain

Ba H_2 O_2

$(137 + 2 + 32 = 171) \div 2 = 85.5$ grams per litre $= 0.085$ gram per c.c.

(The chemical equivalent of barium is half its atomic weight.)

Equal quantities of any normal acid and alkali solution exactly neutralise each other; and the quantity of any solution of a single acid or alkali which is neutralised by 1 c.c. of a normal solution contains 0·001 gram of the hydrogen equivalent of its active constituent. The analyst makes use of a table giving the weights of actual substance in each case, corresponding to the hydrogen equivalent. This is best made clear by an example of such a calculation.

300 c.c. of a solution of caustic soda containing 40 grams of NaHO per litre (normal solution) is required to neutralise 100 c.c. of sulphuric acid and the same volume of nitric acid. Calculate the amount of acid in each solution.

Our previous calculations show that normal sulphuric acid contains 0·049 grams per c.c. As the quantity being tested, 100 c.c., contains acid equal to 300 c.c. of normal alkali, the total quantity present is evidently

$$0.049 \times 300 = 14.7 \text{ grams of sulphuric acid.}$$

Normal nitric acid must have the following composition :—

H N O_3

$1 + 14 + 48 = 63$ grams per litre $= 0.063$ gram per c.c.

Therefore $0.063 \times 300 = 18.9$ grams of nitric acid in the 100 c.c. of solution tested.

CHAPTER IX

OXIDES AND OXY-ACIDS OF CHLORINE

THE following oxides of chlorine have been obtained:

Hypochlorous anhydride, or chlorine monoxide	Cl_2O.
Chlorous anhydride	Cl_2O_3.
Chlorine peroxide	ClO_2.

Chlorine forms also the following series of acids:—

Hydrochloric acid	HCl.
Hypochlorous acid	$HClO$.
Chlorous acid	$HClO_2$.
Chloric acid	$HClO_3$.
Perchloric acid	$HClO_4$.

Hypochlorous Anhydride.—Formula, Cl_2O. Molecular weight, 86·70. Density, 43·35. Specific gravity as gas, 3·00. Boiling-point about 5° C.

108. **Preparation.**—On passing dry chlorine through a tube containing thoroughly dried mercuric oxide, HgO, obtained by precipitation of mercuric chloride, $HgCl_2$, by potassium hydrate, KHO, the following reaction occurs.

$$\underset{\text{Mercury oxide.}}{HgO} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Mercury chloride.}}{HgCl_2} + \underset{\text{Hypochlorous anhydride.}}{Cl_2O}.$$

If the escaping gas be passed through a tube embedded in a freezing mixture of ice and salt, the hypochlorous anhydride condenses to a red liquid, which boils at about 5° C., yielding a light yellow gas.

109. **Properties.**—Hypochlorous anhydride is distinguished by the ease with which it is decomposed, with explosion, into chlorine and oxygen. The liquid suffers this change on being gently warmed, and even on the tube containing it being scratched with a file. The gaseous form is slightly yellow in colour, and smells somewhat like chlorine.

Hydrochloric acid gas and chlorine monoxide mutually decompose each other, with the formation of water and free chlorine.

$2HCl$	+	Cl_2O	=	$2Cl_2$	+	$H_2O.$
Hydrochloric acid.		Hypochlorous anhydride.		Chlorine.		Water.

The gas readily dissolves in water to the extent of about 200 volumes, forming in this manner a solution of hypochlorous acid.

Hypochlorous Acid.—Formula, HClO. Molecular weight, 52·33.

110. **Completeness of Chlorine Acid Series.**—It is interesting to note the complete series of acids formed from chlorine. The first of the series, hydrochloric acid, has already received description. It contains no oxygen; following on this we have the oxy-acids commencing with hypochlorous acid, with its one atom of oxygen, and advancing regularly to perchloric acid containing four oxygen atoms.

111. **Preparation.**—Hypochlorous acid is formed when the anhydride is dissolved in water, and may be prepared more readily by agitating chlorine water with precipitated mercuric oxide in slight excess. The following reaction then occurs :—

HgO	+	$2Cl_2$	+	H_2O	=	$HgCl_2$	+	$2HClO.$
Mercury oxide.		Chlorine.		Water.		Mercury chloride.		Hypochlorous acid.

During the reaction the mercury oxide is dissolved, and the colour of the chlorine disappears. On careful distillation a solution of hypochlorous acid free from mercury chloride is obtained.

112. **Properties.**—A concentrated solution of hypochlorous acid is very unstable, decomposing on exposure to light into chlorine and chloric acid. The acid possesses very powerful bleaching properties, and in the form of one or other of its salts has most important industrial applications. On treatment with hydrochloric acid it is decomposed according to the following equation :—

HCl	+	$HClO$	=	H_2O	+	$Cl_2.$
Hydrochloric acid.		Hypochlorous acid.		Water.		Chlorine.

In the chapter on chlorine an explanation of the theory of bleaching is given, in which it is pointed out that the action is due to the liberation of nascent oxygen from water by the chlorine. Gay-Lussac points out that chlorine in the free state has only half the bleaching power it possesses when combined to form hypochlorous acid. An examination of the following equations shows that in the one case two atoms of chlorine liberate two atoms of nascent oxygen, while in the other the same quantity of oxygen is liberated by the one atom of chlorine in hypochlorous acid.

Cl_2	+	H_2O	=	$2HCl$	+	O.
Chlorine.		Water.		Hydrochloric acid.		Nascent oxygen.
		$HClO$	=	HCl	+	O.
		Hypochlorous acid.		Hydrochloric acid.		Nascent oxygen.

113. Hypochlorites.—Bleaching Compounds.—When chlorine gas is led into a cold solution of potassium hydrate, the following change occurs :—

Cl_2	+	$2KHO$	=	KCl	+	$KClO$	+	H_2O.
Chlorine.		Potassium hydrate.		Potassium chlorate		Potassium hypochlorite.		Water.

From this equation it will be seen that the chlorine partly forms a chlorate and partly a hypochlorite of potassium. The liquid thus produced posesses powerful bleaching action, and is known as *Eau de Javelle* from the name of the place where first manufactured.

114. Chloride of Lime, Bleaching Powder.—At present the cheaper base, lime $Ca(HO)_2$, is used instead of potassium hydrate for the formation of a bleaching compound.

Manufacture.—Chlorine prepared by the action of hydrochloric acid on manganese dioxide (Weldon mud), is allowed to pass through a fairly long pipe in which much of the moisture and accompanying hydrochloric acid are deposited. It is then led into a series of chambers built up of Yorkshire flagstones soaked in tar. On the floors of these chambers a quantity of freshly-slaked lime of good quality is spread in a layer of some four or five inches in depth. The lime being in readiness, the chamber doors are fastened, and the chlorine

permitted to enter till the chamber is seen to be full of chlorine by means of windows placed for the purpose. The chlorine escaping from the one chamber is allowed to pass over into the second similar chamber of the series. In about two days the lime will have absorbed most of the chlorine; it is then turned over by workmen and once more subjected to the action of chlorine. Altogether some six days are required before the lime absorbs the maximum amount of chlorine. It should then contain some 35 per cent. of chlorine available for bleaching purposes. For reasons which will be seen hereafter, it is important to prevent the temperature rising during this operation anything above about 50° C. Chloride of lime as thus prepared is a soft, slightly damp, white powder, having a faint, characteristic smell of hypochlorous acid.

Composition and Properties.—Considerable difference of opinion exists as to the composition of chloride of lime. It is, in the first place, not simply a true hypochlorite, $Ca(ClO)_2$, because as such it should contain approximately 50 per cent. of chlorine, whereas some 35–38 per cent. is the maximum quantity the lime can be made to absorb. Either, therefore, a certain quantity of lime must remain in the free state, or a basic compound must be formed. The following equation agrees fairly well with the results obtained in practice, and assumes the formation of a basic hypochlorite :—

$$\underset{\text{Calcium hydrate.}}{3Ca(HO)_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\substack{\text{Calcium basic}\\ \text{hypochlorite.}}}{2Ca(HO)ClO} + \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Water.}}{2H_2O}.$$

The formula shows that this hypothetic basic hypochlorite consists of calcium hydrate with one group of HO replaced by ClO, expressed graphically thus :

$$H—O—Ca—O—Cl.$$

The objection to this hypothesis is that it necessitates the assumption of the presence of a molecule of calcium chloride to two molecules of the hypochlorite in the bleaching powder. Now calcium chloride is one of the most deliquescent substances known, and yet well-made bleaching powder is at the most only very slightly deliquescent. Further, calcium chloride

is soluble in alcohol, but bleaching powder yields only traces of calcium chloride when treated with alcohol as a solvent. Again, carbon dioxide gas completely expels the whole of the chlorine from chloride of lime, while it is without action on solid calcium chloride.

A much more probable explanation is that which assumes that the following change occurs :—

$Ca(HO)_2$	+	Cl_2	=	$CaOCl_2$	+	H_2O.
Calcium hydrate.		Chlorine.		Calcium chloro-hypochlorite.		Water.

The difficulty in this case is that the whole of the lime is not converted, according to this equation; consequently if we accept it as correct it is necessary also to assume that bleaching powder contains free calcium hydrate as well as the so-called calcium chloro-hypochlorite, $CaOCl_2$. Kolbe affirms that dry bleaching-powder is a definite compound of the following composition, $Ca_3(HO)_6Cl_4$; a formula which agrees, it will be noticed, with the assumption that a chloride of calcium hydrate has been formed by the union of three molecules of the hydrate with two molecules of chlorine. The same formula may be written $(CaO)_3(Cl_2)_2,3H_2O$, in which case we have a hydrated chloro-hypochlorite differing only from that previously described in that it contains a higher proportion of lime. It is probable that this chloro-hypochlorite may contain less water in a state of actual combination than is shown in the formula just given. Such, however, does not materially affect this explanation of the constitution of bleaching powder. The formation of bleaching powder may then be thus represented :—

$3Ca(HO)_2$	+	$2Cl_2$.	=	$(CaO)_3(Cl_2)_2,3H_2O$.
Calcium hydrate.		Chlorine.		Chloride of lime.

On the addition of water to dry chloride of lime, it is decomposed according to the following equation :—

$Ca_3(HO)_6Cl_4$	=	$Ca(HO)_2$	+	$CaCl_2$	+	$Ca(ClO)2$	+	$2H_2O$.
Chloride of lime.		Calcium hydrate.		Calcium chloride.		Calcium hypochlorite.		Water.

On exposure to the air, chloride of lime is slowly decomposed by the carbon dioxide present, free chlorine being evolved :—

$$\underset{\text{Carbon dioxide.}}{3CO_2} + \underset{\text{Chloride of lime.}}{(CaO)_3(Cl_2)_2,3H_2O} = \underset{\text{Calcium carbonate.}}{3CaCO_3} + \underset{\text{Chlorine.}}{2Cl_2} + \underset{\text{Water.}}{3H_2O}.$$

In solution the addition of any acid (including even carbonic acid) causes the evolution of chlorine. Hydrochloric and hypochlorous acids are first evolved, and these mutually decompose each other :—

$$\underbrace{\underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Calcium hypochlorite.}}{Ca(ClO)_2}}_{\text{Active salts of bleaching-powder solution.}} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Calcium sulphate.}}{2CaSO_4} + \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Hypochlorous acid.}}{2HClO}.$$

The secondary reaction is :—

$$2HCl \quad + \quad 2HClO \quad = \quad 2H_2O \quad + \quad 2Cl_2.$$

Industrial Applications.—Chloride of lime is largely used as a disinfectant, the slow evolution of chlorine resulting from its exposure to air rendering it in this respect especially valuable. The principal use of this substance is, as its name implies, that of bleaching. Calico and paper-pulp are both bleached by the action of chloride of lime. The well-washed material is treated with a solution containing about 2 per cent. of bleaching powder, from which it is removed and placed in a dilute solution of either hydrochloric or sulphuric acid. Chlorine is liberated within the fibre of the cloth and destroys the colour. In order to remove all traces of chlorine and acid the cloth is thoroughly washed and finally treated with a solution of sodium sulphite (antichlor), which, by combining with any free chlorine or acid, neutralises their destructive power on the cloth, which otherwise would slowly rot.

Chlorous Anhydride.—Formula, Cl_2O_3. Molecular weight, 118·62. Observed density, 58·73.

Chlorous Acid.—Formula, $HClO_2$. Molecular weight, 68·29.

115. General Properties.—Chlorous anhydride is prepared by the reduction of chloric acid by arsenic trioxide, As_2O_3. It is a gas of a deep greenish-yellow colour and explodes with great readiness. Water dissolves about ten volumes of the gas, forming a solution of chlorous acid. Chlorous acid

possesses bleaching properties, and forms with bases a series of salts known as chlorites. These salts are very unstable, being readily decomposed by heat or by the action of even the most feeble acids. They possess little or no practical interest.

Chlorine Peroxide. — Formula ClO_2. Molecular weight, 67·29. Density, theoretic, 33·64; observed, 33·52.

116. Preparation.—Chlorine peroxide is prepared by gently heating potassium chlorate with concentrated sulphuric acid. Potassium sulphate and chloric acid are first formed, after which the chloric acid suffers decomposition :—

$$\underset{\text{Potassium chlorate.}}{3KClO_3} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} = \underset{\text{Acid potassium sulphate.}}{3KHSO_4} + \underset{\text{Chloric acid.}}{3HClO_3}.$$

$$\underset{\text{Chloric acid.}}{3HClO_3} = \underset{\text{Perchloric acid.}}{HClO_4} + \underset{\text{Chlorine peroxide.}}{2ClO_2} + \underset{\text{Water.}}{H_2O}.$$

The sulphuric acid is first placed in a very small retort and about one-and-a-half times its weight of potassium chlorate added in small quantities at a time. The retort is then gently warmed, and the chlorine peroxide collects as a deep yellow gas. Chlorine peroxide is violently explosive, and for this reason the greatest care is required in its preparation. On being led into a freezing mixture the gas condenses to a dark-red liquid, which at a temperature of $-79°$ C. freezes to a solid mass.

117. Properties.—The gas has a peculiar chlorous odour, and is gradually converted by sunlight into oxygen and chlorine. A very slight elevation of temperature causes its decomposition with violent explosion. Phosphorus and other inflammable bodies burn in the gas spontaneously, at the same time causing it to explode. An interesting experiment of this kind consists in placing a few crystals of potassium chlorate, together with a small fragment of phosphorus, at the bottom of a tall glass filled with water. A thistle-funnel is then placed in the glass and a few drops of sulphuric acid poured down it ; chlorine peroxide is liberated, and each bubble which momentarily comes in contact with the phosphorus explodes with a flash of bright

green light. Chlorine peroxide is soluble in water and thus produces a solution having bleaching powers. The gas is absorbed by a solution of potassium hydrate, but forms no salt corresponding to itself, but simply a mixture of potassium chlorite and chlorate :—

$2ClO_2$	+	$2KHO$	=	$KClO_2$	+	$KClO_3$	+	H_2O.
Chlorine peroxide.		Potassium hydrate.		Potassium chlorite.		Potassium chlorate.		Water.

Chloric Acid.—Formula, $HClO_3$. Molecular weight, 84·25.

118. Preparation.—Chloric acid is best prepared by treating a solution of barium chlorate with the exact quantity of sulphuric acid necessary to form barium sulphate, when the following reaction occurs :—

$Ba(ClO_3)_2$	+	H_2SO_4	=	$BaSO_4$	+	$2HClO_3$.
Barium chlorate.		Sulphuric acid.		Barium sulphate.		Chloric acid.

The insoluble barium sulphate is separated by filtration, and the clear liquid evaporated down *in vacuo* until of a syrupy consistency. It then possesses an intensely acid reaction and has a faint chlorous odour. There is still a considerable quantity of water present, causing the acid of this strength to be approximately represented by the formula $HClO_3,7H_2O$.

119. Properties.—Chloric acid, as thus prepared, is a somewhat unstable body. Any attempts to further concentrate it result in its decomposition into perchloric acid, water, oxygen, and chlorine. It is a very powerful oxidising agent, rapidly charring, and even setting fire to, paper or wood. The acid is monobasic and forms a series of salts known as chlorates.

120. Chlorates.—Among the chlorates the most important is that of potassium, which is prepared in the following manner :—

Preparation.—As previously stated, when chlorine is passed into a cold solution of potassium hydrate, potassium hypochlorite is formed and the liquid possesses bleaching properties. This liquid on being heated is found to lose its

bleaching power, and the hypochlorite is split up into a chlorite and chlorate. Thus in the cold—

$$\underset{\text{Chlorine.}}{3Cl_2} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{6KHO} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{3KCl} + \underset{\substack{\text{Potassium}\\\text{hypochlorite.}}}{3KClO} + \underset{\text{Water.}}{3H_2O}.$$

On the application of heat—

$$\underset{\text{Potassium hypochlorite.}}{3KClO} = \underset{\text{Potassium chlorate.}}{KClO_3} + \underset{\text{Potassium chloride.}}{2KCl}.$$

Grouping the whole chemical change into one equation, we have—

$$\underset{\text{Chlorine.}}{3Cl_2} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{6KHO} = \underset{\substack{\text{Potassium}\\\text{chlorate.}}}{KClO_3} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{5KCl} + \underset{\text{Water.}}{3H_2O}.$$

The chlorate, being much less soluble than the chloride, is readily separated by crystallisation, and forms the very familiar white tabular anhydrous crystals of potassium chlorate. It will be noticed that in this method of manufacture five out of the six molecules of potassium hydrate are converted into the comparatively valueless chloride, a loss which much enhances the price of the chlorate. To avoid this loss, it is usual to first prepare calcium chlorate from lime thus—

$$\underset{\text{Chlorine.}}{6Cl_2} + \underset{\text{Calcium hydrate.}}{6Ca(HO)_2} = \underset{\text{Calcium chlorate.}}{Ca(ClO_3)_2} + \underset{\text{Calcium chloride.}}{5CaCl_2} + \underset{\text{Water.}}{6H_2O}.$$

On adding to this solution the quantity of potassium chloride equivalent to the calcium chlorate, potassium chlorate crystallises out thus—

$$\underset{\text{Calcium chlorate.}}{Ca(ClO_3)_2} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{2KCl} = \underset{\substack{\text{Potassium}\\\text{chlorate.}}}{2KClO_3} + \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2}.$$

In this way the use of the expensive potassium hydrate is avoided.

Properties.—Potassium chlorate, and the chlorates generally, are powerful oxidising agents. All are decomposed on the application of heat, leaving behind a chloride or oxide, and oxygen, or oxygen and chlorine, being evolved. As already known, potassium chlorate is a convenient source of oxygen. Charcoal and most inflammable substances deflagrate when thrown into melted potassium chlorate. Phosphorus and

sulphur both explode when mixed with the chlorate and then subjected to friction or percussion. Chlorates in solution are distinguished from the chlorides by their giving no precipitate with silver nitrate when added to a solution acidulated with nitric acid.

Perchloric Acid.—Formula, $HClO_4$. Molecular weight, 100·21.

121. Preparation.—This acid is most readily prepared from the perchlorate. On heating potassium chlorate until a part of the oxygen is evolved, the liquid is seen to become pasty. If the action be arrested at this stage, it is found that the following change has occurred—

$$\underset{\text{Potassium chlorate.}}{2KClO_3} = \underset{\text{Potassium perchlorate.}}{KClO_4} + \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Oxygen.}}{O_2}.$$

The potassium perchlorate, being much less soluble, is readily separated from the chloride by crystallisation. To prepare the acid, the perchlorate is well dried and mixed with four times its weight of concentrated sulphuric acid. The mixture is subjected to distillation, and there first comes over a slightly yellow liquid, consisting of pure perchloric acid, $HClO_4$. Subsequently portions of the distillate condense into a white crystalline mass, consisting of $HClO_4,H_2O$. On this solid hydrate being redistilled, it is decomposed, and the pure acid first distils over, leaving an aqueous acid, with higher boiling point, behind in the retort.

122. Properties.—Pure perchloric acid is a colourless or slightly yellow liquid, having a great attraction for water. It readily oxidises paper and other organic bodies, while when dropped on charcoal it decomposes with a most violent explosion. The acid gradually undergoes decomposition when kept, and finally acquires a deep red-brown tint and explodes. In the diluted form this acid is the most stable of all the oxy-chlorine acids, and even dissolves iron and zinc, with the formation of perchlorates and evolution of hydrogen.

The salts of perchloric acid are known as perchlorates; they are all decomposed by heat, evolving oxygen and leaving

a chloride. They are more stable than any of the other salts of the oxychlorine series of acids. Perchlorates do not evolve an explosive gas when heated with sulphuric acid.

CHAPTER X

CARBON

Symbol, C. Atomic weight, 11·97. Specific gravity, as diamond, 3·3 to 3·5.

123. **Occurrence.**—Two well-marked crystalline modifications of carbon occur naturally in the free state, being known respectively as diamond and graphite. In addition to these, carbon is an essential constituent of all compounds of organic origin, from which bodies it may be obtained in the amorphous condition; such carbon is termed charcoal or coke, according to the source from which derived. Limestone, chalk, and other natural carbonates also contain carbon in enormous quantities.

124. **Preparation.**—By heating wood, coal, or bones in a closed vessel, carbon in an impure state may be obtained. Water and volatile compounds of carbon with hydrogen and oxygen are driven off; the excess of carbon remains, together with the non-combustible portions of the wood or other body.

This process of heating a body and causing its decomposition into gaseous and liquid products in part, which are collected, is termed 'destructive distillation.'

Charcoal is manufactured sometimes in this way in large iron retorts, but more frequently by building a mass of wood faggots, covering them with peat, and making an opening at the top and bottom. The pile is then fired; a portion only of the wood is allowed to burn, and its heat converts the remainder into charcoal.

Coal is subjected to destructive distillation on the large scale for the manufacture of coal-gas; the carbon which

remains in the retort is known as 'coke.' It is denser and harder than wood charcoal.

Bones, on being similarly treated, yield 'animal charcoal.' This, when finely ground, is called 'ivory black.'

A purer form of charcoal is obtained by burning turpentine, resin, or other substances rich in carbon. With a limited supply of air the hydrogen burns, and the carbon, being liberated, is deposited as soot in chambers arranged for its collection. In this way lampblack is made. It, however, still contains hydrogen, which is driven off by heating the lampblack intensely in a current of chlorine. Hydrochloric acid is formed and carbon remains. The carbon obtained by the whole of these methods is amorphous; graphite and diamond are both crystalline. Graphite occasionally crystallises out in small hexagonal plates from the solution of carbon in fused cast iron. Chemists have long sought to obtain crystals of diamond by artificial means, but hitherto without success.

125. Properties.—The three forms in which carbon occurs differ remarkably in appearance and physical properties.

Diamond.—The diamond is usually found in more or less rounded pebbles, and at times in well-developed octahedral crystals, of the cubical system. The faces of these crystals are frequently somewhat curved, and even the whole form of the crystal distorted. Little is known of the origin or mode of formation of the diamond, except that it has not been produced under the influence of heat. Most diamonds are found in the broken-down *débris* of a fine-grained quartzose rock, but occasionally minute crystals have been found embedded in the rock itself. The diamond is the hardest substance known, scratching or cutting all other bodies. Small crystals, set in a proper holder, are used by glaziers for cutting glass. When pure, the diamond is perfectly transparent and colourless; but many specimens are coloured various shades of yellow to brown, while occasionally diamonds are discovered of a more or less blue tint. By friction against a surface embedded with diamond dust the diamond may be slowly ground down and

caused to take a very high polish. The index of refraction is extremely high, and, in consequence, much of the light which enters the stone undergoes total reflection from the further surface and again emerges. This is one cause of its great brilliancy when cut and used as a gem. The diamond conducts neither heat nor electricity. At the temperature of melting cast iron it remains unchanged, but in the intense heat of the voltaic arc it swells up, becomes opaque, and is changed into a black coke-like mass, and acquires the power of conducting heat and electricity.

Graphite.—Graphite differs from the diamond in almost every characteristic. It occurs in large compact masses in clay-slate, gneiss, and other metamorphic rocks. In some specimens a very distinct crystalline form is observable. These crystals appear as thin hexagonal plates, and belong either to the hexagonal or monoclinic system. Graphite has a metallic lustre and is of a leaden grey colour; in consequence of its similarity to lead it has also received the names plumbago and blacklead. Graphite has a peculiar slippery or greasy feel, owing to the fact that its particles rub off very easily, and exhibit but little friction against each other. It is in consequence largely used as a lubricating agent, having over oil the advantage that it is not wet, and also that it is unaffected by the action of heat. It is very soft and marks paper, hence its employment in the manufacture of blacklead pencils. Graphite is a remarkably good conductor of heat and electricity.

A mixture of graphite and fire-clay is largely used for the manufacture of crucibles for melting cast steel and other metallurgical purposes. These crucibles conduct heat readily, do not easily crack, and allow the metal to pour very freely.

Graphite is almost invariably associated with certain natural impurities, among which are alumina, silica, and iron oxide. In addition about 1 per cent. of hydrogen is usually present.

On gently heating graphite with a mixture of potassium chlorate and sulphuric acid, and then washing the product, a substance remains which contains, in addition to carbon, the elements hydrogen and oxygen, together with some of the sulphuric acid employed in its manufacture. This substance

may be further purified and freed from the sulphuric acid, in which case it forms yellow silky plates, and may be represented by the formula $C_{11}H_4O_5$. In this form it has received the name of graphic acid. On heating this substance it swells up, evolves oxygen and hydrogen, and leaves a mass of finely powdered and pure graphitic carbon.

Amorphous Carbon, Charcoal.—One of the most remarkable properties of charcoal is that which it possesses of absorbing and condensing gases within its pores. Freshly burned charcoal is in this way capable of absorbing about ninety volumes of ammonia. Owing to this peculiar property charcoal is a valuable antiseptic; it absorbs various putrefactive gases, and thus brings them into contact with oxygen, also condensed within it. Oxidation proceeds, and these gases, which are mostly composed of hydrogen and carbon, are changed into harmless and odourless compounds, viz. water and carbon dioxide.

Trays of charcoal are for this purpose placed about in the wards of hospitals; also charcoal air-filters are fixed over the ventilating openings of sewers in order to prevent the escape of noxious gases. When kept dry charcoal will thus continue active for years.

Charcoal also possesses the power of withdrawing certain matters from solution in water and other liquids. Among these are many forms of colouring matter, certain bitter principles, and also the higher alcohols. Thus if port wine or claret be shaken with charcoal and filtered, the resultant liquid is almost colourless. Animal charcoal contains a considerable quantity of inorganic matter derived from the bones; in consequence the charcoal particles themselves are extremely finely divided, and hence animal charcoal possesses greater decolourising power than that prepared from wood. Wood charcoal is largely used for removing the fusel oil (impure amylic alcohol) from distilled spirits; while raw sugar is decolourised by the use of wood charcoal. Charcoal is also employed in the manufacture of water-filters. In a suitable layer it acts mechanically as a filter, and its peculiar absorptive powers enable it to withdraw and retain objectionable matters from the water. It is necessary,

however, that the charcoal be frequently replaced, as when saturated with impurity it may further contaminate, rather than purify, the water passed through it.

In the form of lampblack, charcoal is used as the basis of printers' ink and other black pigments.

Another most important use of charcoal is in the manufacture of gunpowder.

126. Common Chemical Properties.—It is commonly stated that all forms of carbon are incapable of liquefaction or volatilisation at the most intense heats at our command; but Despretz found that the heat produced by the passage of a voltaic current from a battery of 600 Bunsen cells, between carbon points enclosed within an exhausted receiver, volatilised a portion of the carbon as a black cloud, which deposited itself in a crystalline form on the glass walls of the vessel. All varieties of carbon are combustible; and the same weight of diamond, graphite, and charcoal yields the same amount of carbon dioxide when burned, thus establishing their chemical identity:—

$$\underset{\text{Carbon (diamond, graphite, or charcoal).}}{C} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Carbon dioxide.}}{CO_2}.$$

The diamond may be burned by placing it on a connecting strip of platinum foil, between two copper wires passing through the stopper of a gas jar filled with oxygen. The passage of a voltaic current raises the platinum to a white heat, the diamond burns away, leaving only a minute trace of ash.

Graphite in the massive form may be burned more easily. On raising a deflagrating spoon filled with graphite to a white heat, and then plunging it into a jar of oxygen, combustion ensues, and the graphite is converted into carbon dioxide, leaving, however, considerably more ash than does the diamond.

Charcoal, on being heated sufficiently to commence glowing, burns in oxygen with brilliancy.

As a means of detecting carbon dioxide in the resultant gas, use is made of the fact that lime-water is turned milky by the action of carbon dioxide. Lime and carbon dioxide com-

bine readily and produce an insoluble substance, carbonate of lime; hence the milkiness. After a time this falls to the bottom as a white precipitate.

CaH_2O_2	+	CO_2	=	$CaCO_3$	+	H_2O.
Calcium hydrate (lime-water).		Carbon dioxide.		Calcium carbonate (carbonate of lime).		Water.

From this property lime-water is a most useful test for the presence of carbon dioxide. If the carbon dioxide is in considerable excess the precipitate will re-dissolve.

Bodies containing carbon also yield carbon dioxide when burned. Thus, during the burning of a taper, methylated spirits, wood, coal, or coal gas, or petroleum, carbon dioxide is being evolved, and may be detected by the lime-water test. Water is also formed as a product of combustion of these bodies, all of which are compounds containing carbon and hydrogen. The formation of water is demonstrated by the quantity deposited when a cold body is placed above a gas flame. This may be observed whenever a flask of water is heated over a bunsen. Water would also be deposited on the outside of a flask held over the chimney of a petroleum lamp. The carbon compounds with hydrogen are so universally used as heat-producers that no fuel could be taken which did not give these reactions.

127. Production of Animal Heat.—Further, animal heat is also a result of the slow combustion of compounds of carbon. That articles of food contain carbon may be easily demonstrated by heating them to redness in a closed test-tube, when a mass of more or less pure carbon remains. The carbon of food is assimilated by the stomach and helps to build up the body. During the act of breathing, air is drawn into the lungs, and there oxidises certain constituents of the blood, which are obtained from food. Water and carbon dioxide are thus produced, and are exhaled continually from the lungs. Their presence is readily demonstrated, first by breathing against a cold surface, when moisture is deposited, and secondly by breathing through a glass tube into some clear lime-water, which immediately is turned milky.

Carbon dioxide is always present in the atmosphere as a result of the burning of carbonaceous substances and the breathing of animals. Its presence may be detected by exposing a vessel of lime-water to the air, when a thin film of calcium carbonate forms on the surface. As air naturally contains carbon dioxide it might be objected that when one breathes into lime-water, the milkiness is simply due to the naturally contained carbon dioxide, and not to an actual exhalation from the lungs. But that air contains far more carbon dioxide when exhaled from the lungs than when inspired may be proved by the following experiment :—Let two wash-bottles be fitted up respectively with long and short glass tubes, as shown in fig. 35. By means of india-rubber tubing connect one end of a T or three-way tube with the long tube of one of the wash-bottles, and the second end of the T-tube with the short tube of the other wash-bottle. About a quarter fill each wash-bottle with lime-water, and insert the corks. Place the third limb of the T-tube in the mouth and breathe; as each breath is drawn in, air enters through the short-limbed wash-bottle, bubbling through the lime-water. At each exhalation air passes out through the other bottle. The air is thus passed through lime-water before and after being breathed. The lime-water in the first bottle is only rendered very slightly turbid; that in the second rapidly becomes milky.

FIG. 35.

128. Reducing power of Carbon.—Although carbon does not take fire at anything like so low a temperature as phosphorus and many other substances, it is yet a most powerful reducing agent. Its vigour as such increases with the temperature. At a bright red heat it decomposes phosphorus compounds, with the liberation of free phosphorus. Carbon also reduces, at a high temperature, the compounds of sodium and potassium, and thus enables those elements to be obtained in the metallic state. In the procuring of most metals from their ores, carbon not only acts as a fuel, producing the requisite amount of heat, but also serves as a reducing agent,

combining with the oxygen or other element with which the metal is united in the ore.

129. Industrial uses of Carbon.—Reference has been incidentally made to these when describing the various allotropic forms of this element; they may, however, be recapitulated here.

Diamond.—Used as a gem, and for cutting glass; coarser forms employed as the cutting agent in rock-boring implements.

Graphite.—Used in the manufacture of blacklead pencils; also as a lubricant, and for glazing gunpowder. Graphite is employed as a protective coating for ironwork, as when used for blackleading stoves.

Charcoal.—Charcoal and coke are both largely used as fuel, and as reducing agents in metallurgical operations. Charcoal acts as a deodorising and decolourising agent, and is used for filtering and other purifying purposes.

130. Compounds of Carbon.—Carbon is distinguished among the elements by the great number of compounds it is capable of producing by its union with comparatively few elements. The number of carbon compounds obtainable from the union, in various proportions, of two or more of the four elements, carbon, hydrogen, oxygen, and nitrogen, is incalculable. They of themselves are of such importance as to constitute a division of chemistry, almost, if not quite, equal in extent to the chemistry of all other elements together. These carbon compounds have been principally obtained from either animal or vegetable sources, and consequently the section of chemistry which makes them its subject is commonly called 'organic' chemistry, as distinguished from inorganic chemistry, which deals only with bodies whose origin and production is independent of the action of vital functions. Of late years, many substances have been produced by direct synthesis of the elements which previously had only been obtained from organic sources; therefore the line of demarcation between the two divisions of the science has been and is being gradually broken down. As a matter of convenience, however, the distinction is still retained,

and accordingly descriptions of these carbon compounds will be found in treatises specially devoted to that subject. A few only of the simplest and most important will receive treatment in this work.

CHAPTER XI

OXIDES OF CARBON

Two oxides of carbon are known :—

Carbon monoxide or carbonic oxide, CO.
Carbon dioxide or carbonic anhydride, CO_2.

The latter of these, being the most important, should be first studied.

Carbon Dioxide.—Formula, CO_2. Molecular weight, 43·89. Density, 21·94. Specific gravity, 1·527.

131. **Occurrence.**—The presence of carbon dioxide in the atmosphere is mentioned in the previous chapter; it also exists in vast quantities in combination with lime, in limestone, chalk, marble, &c.

132. **Preparation.**—By the action of heat, limestone may be decomposed into lime and carbon dioxide, according to the following equation :—

$$\underset{\text{Limestone (calcium carbonate).}}{CaCO_3} = \underset{\text{Lime (calcium oxide).}}{CaO} + \underset{\text{Carbon dioxide.}}{CO_2}.$$

Enormous quantities of limestone are 'burned' in properly constructed furnaces called kilns, for the purpose of obtaining quicklime, that substance being used in making mortar. The change which occurs is that shown in preceding equations quicklime being simply another name for calcium oxide.

A much readier method of separating the carbon dioxide from the base is by the addition of an acid, as hydrochloric. The following change ensues :—

$$\underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Calcium chloride,}}{CaCl_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide}}{CO_2}.$$

This reaction occurs in the cold, and the gas is prepared for laboratory use in this manner, simply by placing a few fragments of marble in a flask fitted with thistle-funnel and delivery-tube, and then adding the acid through the funnel. To purify the gas it should be passed through water in a small wash-bottle. Carbon dioxide may be collected over water or by downward displacement.

133. Manufacture.—On the large scale carbon dioxide may be prepared by burning charcoal or coke, or by heating limestone. It is commonly prepared by the aërated water manufacturers from precipitated calcium carbonate (whiting) and sulphuric acid. The whiting, together with water, is placed in a closed vessel, and sulphuric acid gradually added. Within the vessel a spindle fitted with iron arms is placed, and this by revolving brings the whole of the mixture in contact with the acid and ensures uniformity of evolution of gas. The great cheapness of sodium bicarbonate is now causing it to be used largely as a substitute for whiting. It has the great advantage of producing a soluble bye-product.

134. Properties.—Carbon dioxide is a colourless gas. It has a faint, sweetish, acid taste and smell, which are best described as being those of a bottle of soda-water when opened (so-called soda-water is a solution of carbon dioxide in water under pressure).

At a pressure of 38·5 atmospheres this gas condenses to a liquid at 0° C. : it may also be liquefied at ordinary pressures by a temperature of $-78°$ C. Liquid carbon dioxide is colourless and transparent ; on being allowed to emerge in a stream from the vessel containing it, a part volatilises, and, in so doing, deprives the remainder of the heat necessary to maintain it in the liquid state ; it therefore freezes. The solid carbon dioxide gas obtained in this manner is a white, snow-like mass which evaporates with comparative slowness. Liquid carbon dioxide has no very energetic chemical properties, and is without action on litmus paper. It has a remarkably high co-efficient of expansion, and increases in volume more rapidly than does a gas subjected under like conditions to a similar increase

At 15° C. the gas is soluble in about its own volume of water, whatever the pressure; but as an increase of pressure increases the density of the gas, the *weight* absorbed is in direct proportion to the pressure to which the gas is subjected. Soda-water, lemonade, and other aërated beverages, are prepared by dissolving carbon dioxide in water, under the pressure of a force-pump. From the solubility of the gas in water directions are frequently given for its collection by displacement, but the gas is obtained so readily in large quantity that for most purposes it may as well be collected over water.

Owing to its comparatively high density, carbon dioxide has a tendency to accumulate in situations where it is produced in larger quantities than are removed by ordinary processes of gaseous diffusion. Thus in brewing, carbon dioxide is formed in the vats by the decomposition of sugar into this gas and alcohol during fermentation. The vats may remain full of the gas after the liquor has been withdrawn, and many fatal accidents have occurred through men incautiously descending in them. Similar accumulations occur both in disused mines and in deep wells; hence, before they are entered by men it is well to test the air by lowering a lighted taper, which should burn freely.

Carbon dioxide gas is neither inflammable nor, under ordinary circumstances, a supporter of combustion.

Several of the metals, however, which have a great affinity for oxygen burn in the gas, with the displacement of carbon. If a piece of brilliantly burning magnesium wire is introduced into the gas, it continues to burn; the fragments of magnesium oxide falling to the bottom are found mingled with carbon. On the jar being rinsed with a few drops of hydrochloric acid, the oxide dissolves, and the carbon is readily distinguished:—

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Magnesium.}}{2Mg} = \underset{\text{Magnesium oxide.}}{2MgO} + \underset{\text{Carbon.}}{C.}$$

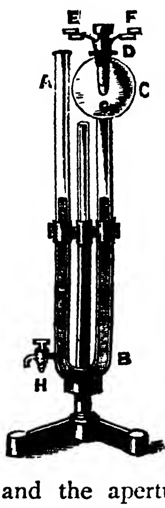
The same reaction is also effected by potassium, potassium oxide being formed instead of that of magnesium. In this latter case, a small dry flask is filled with carbon dioxide by downward displacement; a pellet of potassium about the size of a pea is introduced, and the flask gently warmed until the

potassium glows. The action having terminated, the flask is allowed to cool and its contents dissolved out with water; a residue of free carbon is seen to remain.

Carbon dioxide gas in its pure form causes asphyxia, the glottis being spasmodically closed if an attempt be made to breathe the gas. When present in air to the extent of from 3 to 4 per cent. carbon dioxide acts as a narcotic poison, lowering both the frequency and vigour of the heart's action. Hence the absolute necessity of thorough ventilation of sleeping chambers, and all other rooms inhabited for any length of time by a number of people.

135. Composition.—The exact composition of carbon dioxide, both by weight and by volume, has been made the subject of most careful investigation. The gas contains its own volume of oxygen, a fact which is proved by burning pure carbon in a measured quantity of oxygen gas. For this purpose the apparatus shown in fig. 36 may be employed. A B C is a bent tube open at A, and having a bulb C blown at the other end. To the neck of this bulb at D is fitted a glass stopper, through which pass two wires, E F, suspending a small platinum capsule, G. The apparatus is first filled with mercury, and then oxygen gas passed by means of a tube down A, until the bulb C, and part of the limb B C, are in this manner charged with oxygen. The mercury is then brought to the same level in the two limbs by allowing as much as necessary to escape through the cockstop H. In the next place the stopper at D is removed, and the aperture temporarily closed with a cork. A piece of pure carbon (which may be either of the allotropic modifications) is placed in G, and the stopper quickly replaced. (This operation permits some of the oxygen to escape during the momentary removal of the stopper; where great accuracy is required this may be obviated by fastening the carbon in the capsule by fine platinum wire, prior to filling the apparatus

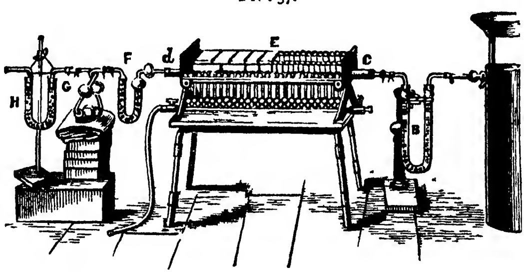
FIG. 36.



with mercury.) The level of the mercury is noted, and then a voltaic current passed, by means of the wires E, F, through the platinum capsule, which is thus raised in temperature to a red heat. The carbon commences to burn, and at the conclusion of the combustion the apparatus is allowed to stand until it once more regains the atmospheric temperature. The volume of carbon dioxide remaining is then found to be the same as that of the oxygen prior to the carbon being burned. A molecule of carbon dioxide is thus shown to be produced for each molecule of oxygen consumed.

The composition of carbon dioxide by weight is determined by passing oxygen over a weighed quantity of red-hot carbon and weighing the resultant carbon dioxide. The following apparatus, fig. 37, is that employed for the purpose. The gasholder A contains pure oxygen, and is connected to the

FIG. 37.



U-tube B, filled with fragments of caustic potash; to this is attached a piece of hard glass (combustion) tubing *c d*, resting in the gas combustion furnace E. Within this tube from the *c* end is inserted an elongated platinum capsule ('platinum boat'), containing either diamond, graphite, or charcoal; the boat and its contents having first been weighed The remainder of the tube toward the end *d* is filled with granulated copper oxide. Prior to the commencement of the experiment the carbon, platinum boat, and copper oxide should be heated until absolutely free from moisture. At the end *d* is fixed a chloride of calcium tube F, and again to this a series of glass bulbs G, partly filled with a concentrated solution of potassium hydrate. Finally, we have a U-tube, H, charged with calcium

chloride. The apparatus F, G, H, are first carefully weighed. Everything being arranged, and all the joints made airtight, a slow current of oxygen is admitted through from the gas-holder; any traces of moisture are removed by the drying-tube B. The gas is then lighted at the *d* end of the combustion furnace, so as to raise the copper oxide to a red heat. As burner after burner of the furnace is lighted the heat approaches the carbon, which on becoming red-hot commences to burn in the atmosphere of oxygen. If any traces of carbon monoxide, CO, are found they are oxidised to CO_2 during their passage through the red-hot copper oxide. There escapes at *d* carbon dioxide gas mixed with the excess of oxygen. Any traces of moisture, either from the carbon or the copper oxide, are absorbed and retained by F. As the gas bubbles through G the carbon dioxide is completely absorbed. The drying-tube H is arranged for the retention of any moisture that might possibly be carried over from the potash bulbs G. The carbon being entirely consumed, the current of oxygen is maintained until the whole of the carbon dioxide is driven out of the tube *cd*; the apparatus is then allowed to cool. The loss in weight of the platinum boat represents the quantity of carbon consumed. The increase in weight of the tubes G and H gives the weight of carbon dioxide produced. The weight of the tube F furnishes a useful check on the freedom, or otherwise, from moisture of the carbon and copper oxide. With an apparatus of this kind Dumas made five combustions of natural graphite, four of artificial graphite, and five of diamond, with the result that 800 parts by weight of oxygen combined with

299·94 parts of natural graphite.
299·95 „ „ artificial „
300·02 „ „ diamond.

From these figures, having a mean of 299·97, it is deduced that 2 atoms of oxygen, weighing 31·92, combine with 11·97 parts of carbon to form carbon dioxide.

136. Industrial Applications.—Carbon dioxide has been employed with considerable success for the purpose of extinguishing fires in underground coal-mine workings.

These, if they take fire, may remain burning for years, and thus be a source of great loss. Such a mine on fire has the whole of its openings stopped save two; one of these is employed as an exit, and through the other air which has passed through a coke fire is forced into the mine. Such air consists of a mixture of carbon dioxide and nitrogen gases, and effectually extinguishes the flame. Carbon dioxide is used, as already stated, in the manufacture of aërated beverages, which consist of either pure water, or water flavoured with various syrups and impregnated with this gas. Carbon dioxide is also almost universally employed for the purpose of aërating bread, being produced either by fermentation within the dough, or added in the form of a solution in water under pressure. Liquid carbon dioxide, owing to its great volatility at low temperatures, is employed as an agent for the production of extreme cold.

137. Carbonic Acid and Carbonates.—Carbon dioxide possesses feebly acid properties when combined with water, and therefore is sometimes called carbonic anhydride. If a solution be made of carbon dioxide in water under pressure, and then the pressure immediately removed, the liquid becomes milky through the escape of minute bubbles of carbon dioxide gas throughout the whole solution. But if the solution is kept for some time and then released from pressure, the carbon dioxide is much more slowly liberated, and in big bubbles which escape at the sides of the containing vessel. The inference is that during the time the liquid has been standing, the mere solution has been changing into a state of chemical combination, according to the equation—

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Carbonic acid.}}{H_2CO_3}.$$

The solution of carbon dioxide in water is therefore viewed as a true acid, although it is impossible to free it from an excess of water. Carbonic acid is very unstable, the gas being entirely expelled from water, either by boiling or freezing.

Carbonic acid changes the colour of a blue solution of litmus to an intermediate port-wine tint, which is very different from the full red colour produced by the stronger acids.

Although carbonic acid is so feeble in character, it nevertheless produces a stable and most important series of salts called carbonates. Being dibasic it forms both acid and normal carbonates; it is also one of those acids which frequently yield basic salts. Thus we have sodium carbonate Na_2CO_3, and sodium bicarbonate, or acid sodium carbonate $NaHCO_3$. White lead $(PbCO_3)_2,Pb(HO)_2$, has already been cited as an instance of a basic salt.

The more vigorous bases, as potassium or calcium hydrates, combine directly with free carbon dioxide, forming carbonates. The already familiar test of carbon dioxide with lime-water depends on the utilisation of this reaction. A similar change proceeds during the setting of mortar, in which the free calcium hydrate slowly combines with carbon dioxide absorbed from the atmosphere. Other metallic hydrates—as, for example, that of copper—do not directly combine with carbon dioxide, but may be caused to form carbonates by the addition of a soluble carbonate to a solution of their salts. These carbonates are easily decomposed; that formed of copper under these conditions, separating into the hydrate and free carbon dioxide at the temperature of boiling water. With the exception of barium carbonate and those of the alkalies, all carbonates are decomposed on ignition into the oxide and carbon dioxide.

The carbonates are all readily decomposed by almost any acid, with evolution of carbon dioxide and formation of a salt of the decomposing acid and the base.

With the exception of those of the alkalies, the whole of the normal carbonates are insoluble in water; the acid- or bicarbonates of the metals of the alkaline earths (calcium, &c.) are soluble, being, in fact, only known in solution. If hard water, obtained from either chalk or other limestone formation, be boiled for from ten minutes to a quarter of an hour, the water will be found to have become slightly turbid, through the separation of calcium carbonate. The change which has occurred may be viewed as the following—

$$\underset{\text{Calcium bicarbonate, soluble.}}{CaH_2(CO_3)_2} = \underset{\text{Calcium carbonate, insoluble.}}{CaCO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2}.$$

The soluble bicarbonate will have been decomposed by the heat, and the insoluble carbonate precipitated. A more complete study of the same reaction is obtained by passing a current of washed carbon dioxide gas into some lime-water in a beaker. At first a precipitate of calcium carbonate is produced; with the continued passage of carbon dioxide this precipitate is re-dissolved, with the formation of the bicarbonate. At this stage, if the liquid be boiled, carbon dioxide is evolved, and the normal carbonate again precipitated. Instead of assuming that a soluble bicarbonate is formed by the continued passage of carbon dioxide, as just described, it is sometimes stated that calcium carbonate is soluble in excess of carbonic acid. Solubility in such a case is, however, most probably due to the formation of a bicarbonate as explained.

138. Hard and Soft Waters.—In the preceding paragraph reference has been made to 'hard water'; the inference may be drawn that hardness is in some way connected with the presence of calcium salts in solution. It may be well to explain here what is understood by the terms 'hard' and 'soft' when applied to water, and to what these properties are due. Certain kinds of water when mixed with a very small quantity of soap immediately produce a lather, and the water acquires that peculiar feel to the hands known as 'soapiness.' Such water is termed 'soft.' Other waters when used with soap for washing purposes do not lather at all readily, and do not cause 'soapiness' until a considerable quantity of soap has been consumed. When a lather is actually formed, there will be found on examination a layer of scum on the surface of the water. Such water is termed 'hard.'

Without going into the details of the composition of soap and its reaction with water when used for washing, it may be explained that soluble salts of calcium and magnesium decompose soap, forming a precipitate which constitutes the previously mentioned scum found when washing with hard water. Consequently, if water containing calcium salts in solution is employed for washing, sufficient soap must first be added to precipitate these salts before any is available for

cleansing; hence hard waters are neither so agreeable nor so economical for washing purposes.

The principal calcium and magnesium salts found in water are the carbonate and the sulphate. As seen from a previous experiment, the carbonates may be precipitated by the act of boiling, and any hardness due to their presence may be thus remedied. **Consequently any hardness produced by carbonates of calcium or magnesium is termed 'temporary' hardness, because such hardness is removed by boiling.**

The sulphates and chlorides of calcium and magnesium are not precipitated by boiling, as their solution is caused by the water itself, and not by water plus carbon dioxide gas. **Therefore hardness due to the presence of sulphates (or chlorides) of calcium or magnesium is termed 'permanent' hardness.**

The hardness of most waters is partly temporary and partly permanent; the two together constitute the total hardness of the water.

The hardness of water is usually tested by taking a measured quantity of the water and adding thereto in a stoppered bottle a solution in alcohol of soap of a known strength. This is introduced in small quantities at a time from a measuring instrument, the water being well shaken after each addition. As soon as a lather is thus produced, which stands unbroken for five minutes, the quantity of soap solution which has been used is read off; from these data, the total hardness is determined. A sample of the water is next boiled until the carbonates are precipitated; then, after certain precautions, the hardness is again determined with the soap solution. This gives the permanent hardness; the difference between the total and the permanent is the temporary hardness.

139. Processes of Softening Water.—Water may be softened to the extent of the removal of the temporary hardness by the act of boiling for some minutes. Potassium and sodium carbonates precipitate calcium and magnesium salts, and them-

selves possess detergent or washing properties; therefore these salts will remove all hardness, whether temporary or permanent. One of the characteristics of potassium and sodium carbonates is the power they possess of imparting a soapy feel to pure water. Ordinary washing soda, or soda-crystal, is commercial sodium carbonate.

140. Clark's Water-softening Process.—A most interesting process for the softening of water is that bearing the name of Clark's process. The process depends on two chemical reactions with which the student is already familiar. First, that calcium carbonate is no longer soluble in water from which the carbon dioxide gas has been removed; secondly, that lime forms an insoluble compound with carbon dioxide gas. To soften water by Clark's process, lime-water is added in sufficient quantity to exactly combine with the dissolved carbon dioxide gas. The whole of the lime, both that originally present in the water as carbonate and that added as hydrate, is precipitated, and the temporary hardness of the water is thus removed. The chemical reaction is represented in the following equations:—

$$\left\{\begin{array}{l} CaCO_3 \\ H_2O,CO_2 \end{array}\right. \begin{array}{cccccc} & & = & CaCO_3 & & \\ + & CaH_2O_2 & = & CaCO_3 & + & 2H_2O. \end{array}$$

Solution of carbon dioxide in water (carbonic acid) holding calcium carbonate in solution.	Lime water (calcium hydrate).	Original calcium carbonate, and also that formed from dissolved carbon dioxide and added calcium hydrate. Both insoluble.	Water.

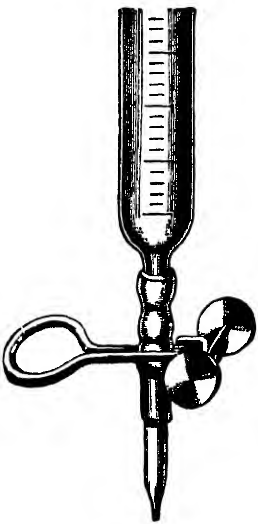
The precipitated lime is removed either by allowing it to subside or by filtration.

The phenomena of temporary and permanent hardness, and also the various water-softening processes, may be further elucidated by the performance of the following series of experiments. Procure some standard soap solution, such as is used for water analysis. (This may be prepared in the laboratory, according to directions given in works on analysis, or may be purchased from dealers in chemicals.) The following apparatus will be required: a burette, holding 50 c.c., and

stand; the end of a burette is shown in the accompanying figure. The instrument consists of a glass tube, graduated throughout most of its length, and with a spring clip arranged at the bottom. A pipette, holding 50 c.c., and a stoppered bottle, of about ten ounces capacity, are also requisite.

Having cleaned the various apparatus, place the lower end of the pipette in some hard water and suck it up above the level of the graduated mark round the stem. Place the thumb on the top, and let the water drop slowly from the bottom until the graduation mark is exactly reached. Then, by removing the thumb, allow the whole of the contents of the pipette to drain into the bottle. Rinse the burette with a few drops of the soap solution and then fill it above the zero mark at the top. Press the buttons of the spring clip and allow the solution to run out until the zero line is reached. Next run the soap solution into the hard water in the bottle in quantities of about 1 c.c. at a time, shaking vigorously between each addition, and noticing whether or not any signs appear of a permanent lather being formed.

FIG. 38.—BURETTE WITH SPRING CLIP.



Continue this until, when the bottle is shaken and laid on its side, the lather does not break for five minutes. Make a note of the quantity of soap solution which has been used.

Next take a light flask of about 250 c.c. capacity: place it on a balance and fill with the water until the water and flask together weigh exactly 200 grams. Set the flask over a Bunsen burner and boil the water for half-an-hour. At the end of that time place the flask again on the balance and make up to the weight of 200 grams by adding recently boiled distilled water. This is done in order to replace the water lost by evaporation. Filter off the precipitated calcium carbonate, let the water cool,

and determine the hardness in 50 c.c. precisely as before. The hardness now found is the permanent; that which has disappeared through boiling is the temporary.

To another portion of the hard water add sodium carbonate (washing soda) until the water feels soapy to the touch; then test with soap solution, and notice that a lather is produced by the addition of the first few drops.

Prepare a solution of phenolphthalein by dissolving 1 gram of the substance in 30 c.c. of strong alcohol. Take a litre of the hard water; add a few drops of the phenolphthalein solution and then pour in lime-water until the water acquires a faint pink tint. From 80 to 100 c.c. of lime-water will probably be required. (The object of the phenolphthalein is to show the point when a sufficient quantity of lime has been added, as the slightest excess causes in the presence of this substance a red colouration.) The pink tint may be again discharged by the cautious addition of a little more of the water until the colour just disappears. Let the water stand for a few hours, and a precipitate of calcium carbonate falls to the bottom. Determine the hardness of the clear water; it should closely agree with that softened by boiling.

In softening water on the large scale the testing with phenolphthalein is performed, not on the whole bulk, but on small quantities taken out from time to time for the purpose of making the test.

•Carbon Monoxide. — Formula, CO. Molecular weight, 27·93. Density, 13·96. Specific gravity, 0·967.

141. Occurrence.—Carbon monoxide does not occur in the free state in nature, but is largely produced during the combustion of carbon in an incomplete supply of air. Thus, when a coke or charcoal fire is glowing with a bright red heat, lambent blue flames may be seen hovering over the top. These are due to the combustion of carbon monoxide, formed within the burning mass of coke. It may be assumed that at the lower part of the fire, where an upward current of air

enters, carbon dioxide is formed according to the following equation :—

$$\underset{\text{Carbon.}}{C} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Carbon dioxide.}}{CO_2}.$$

This makes its way upwards through the red-hot carbon and becomes changed by reduction to carbon monoxide, and thus an inflammable gas is produced. That this change occurs may readily be proved by passing a current of carbon dioxide gas through a red-hot iron tube packed with fragments of charcoal. The issuing gas burns with a blue flame, and is produced according to the following equation :—

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Carbon.}}{C} = \underset{\text{Carbon monoxide.}}{2CO}.$$

142. Preparation.—In addition to the reaction just described, carbon monoxide may be prepared by heating within an iron tube a mixture of chalk (calcium carbonate) and charcoal. The chalk is decomposed into calcium oxide and carbon dioxide, which latter is converted by the charcoal into the monoxide.

A mixture of carbon monoxide and free hydrogen is produced in abundance by passing steam over or through charcoal heated to bright redness :—

$$\underset{\text{Carbon.}}{C} + \underset{\text{Water.}}{H_2O} = \underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Hydrogen.}}{H_2}.$$

For laboratory purposes the gas is most conveniently prepared by heating certain organic compounds with concentrated sulphuric acid. This body has a very great attraction for water, in virtue of which it decomposes many substances containing hydrogen and oxygen, and assimilates the water ; the remaining atoms re-arrange themselves into whatever other compounds are possible. Oxalic acid, when thus treated, is split up into water, carbon dioxide, and carbon monoxide :—

$$\underset{\text{Oxalic acid.}}{H_2C_2O_4} = \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Carbon monoxide.}}{CO}.$$

Equal volumes of carbon monoxide and dioxide are thus produced. Pure carbon monoxide may be obtained by passing the evolved gas through one or more wash-bottles containing a

concentrated solution of caustic potash, by which all carbon dioxide may be absorbed, with the formation of potassium carbonate.

Formic acid, on being similarly heated with concentrated sulphuric acid, yields pure carbon monoxide, according to the following equation :—

$$\underset{\text{Formic acid.}}{HCHO_2} = \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon monoxide.}}{CO.}$$

Another method is to heat potassium ferrocyanide (yellow prussiate of potash) with sulphuric acid ; the change occurring is complicated :—

$$\underset{\text{Potassium ferrocyanide.}}{K_4FeC_6N_6} + \underset{\text{Sulphuric acid.}}{6H_2SO_4} + \underset{\text{Water.}}{6H_2O} =$$

$$\underset{\text{Potassium sulphate.}}{2K_2SO_4} + \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Ammonium sulphate.}}{3(NH_4)_2SO_4} + \underset{\text{Carbon monoxide.}}{6CO.}$$

When the monoxide is required in a state of absolute purity the former of these two reactions is the preferable. The latter yields the gas in large quantities, but usually accompanied by traces of carbon dioxide as an impurity. With the ferrocyanide no gas is evolved until the mixture is heated to a high temperature ; but when the evolution of gas once commences, it proceeds with very great rapidity. Hence it is necessary to use a large flask provided with wide delivery-tubes.

143. **Properties.**—Carbon monoxide is a colourless gas ; it has a slight oppressive odour, and is extremely poisonous, producing a painful headache even when present in small quantities in air. It is but slightly soluble in water : 100 volumes dissolves 2·434 volumes of the gas at 15° C. It liquefies only under very great cold and pressure. Carbon monoxide is inflammable and a non-supporter of combustion ; when burned its own volume of carbon dioxide is produced, half of its volume of oxygen being required :—

$$\underset{\text{Carbon monoxide.}}{2CO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Carbon dioxide.}}{2CO_2.}$$

This gas is devoid of acid properties, and consequently is without action on lime-water ; so that if a jar of carbon mon-

oxide have some lime-water added and then be shaken, no turbidity is produced. But if a light be applied, and then, when the combustion is completed, the jar again be shaken, the lime-water is turned milky by the carbon dioxide formed by the burning of the gas.

Carbon monoxide acts as a powerful reducing agent, and is frequently used in metallurgical operations for the production of metals from their oxides. Thus on passing carbon monoxide over red-hot copper oxide, reduction occurs with the formation of carbon dioxide :—

$$\underset{\text{Copper oxide.}}{CuO} + \underset{\text{Carbon monoxide.}}{CO} = \underset{\text{Copper.}}{Cu} + \underset{\text{Carbon dioxide.}}{CO_2}.$$

Owing to the carbon of carbon monoxide having an unsaturated valency of two, this compound enters very readily into further combination. Thus, as we have seen, the dioxide is readily formed by its union with an extra atom of oxygen under the influence of sunlight ; carbon monoxide unites with an equal volume of chlorine, forming *carbonyl chloride*, or *phosgene* gas :—

$$\underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Phosgene gas.}}{COCl_2}.$$

Carbon monoxide also enters directly into combination with potassium hydrate when heated with it, forming potassium formate :—

$$\underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Potassium hydrate.}}{KHO} = \underset{\text{Potassium formate.}}{KCHO_2}.$$

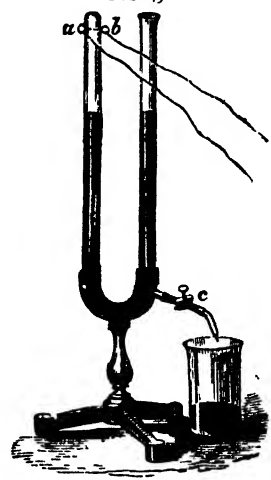
144. Industrial Applications. — Indirectly, carbon monoxide, as just stated, fulfils important functions in various metallurgical operations. Thus, in roasting copper ores at Swansea, anthracite coal is used. This form of coal is approximately pure carbon, and when burned in the furnace yields carbon monoxide, which in passing over the ore exerts a reducing action.

In iron-smelting by means of the blast furnace, enormous volumes of carbon monoxide are formed, and formerly used to burn at the top of the furnace. This carbon monoxide is now

collected and used as a fuel for the purpose of heating the air employed as a hot blast.

145. Composition.—The composition of carbon monoxide by volume may be determined by means of the eudiometer shown in fig. 39. Into this eudiometer a given quantity—say twenty volumes—of carbon monoxide is introduced. In every case, prior to reading the volume, the mercury in the two limbs must be brought to a level, either by adding through the top of the right-hand limb or withdrawing some of the metal by means of the stop-cock *c*. In the next place, twenty volumes of pure oxygen are added, the open end is firmly closed with the thumb, and an electric spark passed through the wires *a*, *b*. The forty volumes of gas will now be found to have become thirty volumes. A small quantity of potassium hydrate solution must be added; this will absorb the carbon dioxide formed, and a diminution of twenty volumes will result. The remaining ten volumes consist of oxygen, a fact which may be proved by the addition of pyrogallic acid, by which, in the presence of potassium hydrate, oxygen is rapidly and completely absorbed. We thus find that twenty volumes of carbon monoxide have combined with ten volumes of oxygen, and have produced twenty volumes of carbon dioxide. This fact agrees with the molecular equation already given.

FIG 39



CHAPTER XII

HYDROCARBONS AND COMBUSTION

146. Hydrocarbons.—The compounds of carbon with hydrogen are known as hydrocarbons, or hydrides of carbon. These bodies are exceedingly numerous, and as most of them are distinctly of organic origin, their study is usually undertaken as a part of organic rather than inorganic chemistry. Only the following simple and important hydrocarbons will receive attention in this work :—

Marsh Gas, Light Carburetted Hydrogen, or Methyl Hydride . . . . CH_4.
Acetylene . . . . C_2H_2.
Olefiant Gas, Heavy Carburetted Hydrogen, or Ethene . . . . C_2H_4.

Marsh Gas, Methyl Hydride.—Formula, CH_4. Molecular weight, 15·97. Density, 7·98. Specific gravity, 0·551.

147. Occurrence.—This gas is evolved during the decomposition of dead vegetable matter; hence is found in marshy districts, and has thus received its common name of marsh gas. On watching stagnant water, bubbles of the gas may be seen to arise, and may be collected by inverting a gas jar, filled with water, in the pool. During the changes which have occurred, as coal has been formed from vegetable growths, marsh gas has also been evolved, and has remained imprisoned within cavities of the coal itself. As the coal is removed by the miner, the gas escapes from these cavities into the mine, and mixing with the air forms the explosive mixture which has been the cause of so many terrible colliery accidents. The collier knows this gas as 'fire-damp.'

148. Preparation.—Marsh gas may be prepared by heating together a mixture of sodium acetate and caustic soda, when the following reaction occurs :—

$$\underset{\text{Sodium acetate.}}{NaC_2H_3O_2} + \underset{\text{Caustic soda.}}{NaHO} = \underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Marsh gas.}}{CH_4}.$$

For this purpose it is well to employ, as a retort, an iron tube closed at one end. The open end is fitted with a cork and delivery-tube from which the escaping gas is collected.

149. Properties.—Marsh gas is a light, colourless gas, and has consequently received the name of light carburetted hydrogen. It is not a supporter of combustion, but burns with a non-luminous flame, something like that of hydrogen, but slightly tinged with yellow. Mixtures of either air or oxygen with this gas explode violently on ignition, carbon dioxide and water being formed as products of the combustion or explosion. The carbon dioxide thus produced from marsh gas is known by the miner as 'choke-' or 'after-damp.'

Until recently, marsh gas was viewed as a permanent gas, but, in common with hydrogen and other gases, has now been liquefied.

150. Composition by Volume.—The composition of this gas may be ascertained by explosion with excess of oxygen in the eudiometer. If ten volumes of marsh gas be mixed with twenty-five volumes of oxygen there will be found, after explosion, at a temperature above 100° C., thirty-five volumes of gas. On cooling to normal temperature the volume of gas contracts to fifteen; there must therefore have been present twenty volumes of water vapour. On introducing caustic potash a further absorption of ten volumes occurs, showing that ten volumes of carbon dioxide have been formed. The residual five volumes of gas are found on examination to be oxygen. One volume, therefore, of this gas requires for its combustion two volumes of oxygen, and produces one volume of carbon dioxide and two of water vapour.

Remembering that by Avogadro's law the molecular volume of all gases is alike, and that the molecule of hydrogen contains two atoms, then as two volumes of the gas yield two volumes of carbon dioxide, or one molecule yields a molecule of carbon dioxide, one molecule of marsh gas contains one atom of

N 2

carbon. Again the two volumes of marsh gas produce four volumes of water vapour—that is, one molecule of marsh gas yields two molecules of water; and as each molecule of water contains two atoms of hydrogen, the molecule of marsh gas contains four atoms of hydrogen; the formula must consequently be CH_4.

151. Composition by Weight.—The composition by weight is ascertained by passing a known volume of marsh gas through a combustion-tube containing red-hot copper oxide. Carbon dioxide and water are formed, and are absorbed in weighed tubes containing respectively calcium chloride, which absorbs the water, and caustic potash, by which the carbon dioxide is retained. The increase in weight gives the amounts of these two bodies formed from the marsh gas. In an experiment a volume of CH_4, equivalent to 1000 c.c. at N.T.P., was passed over red-hot copper oxide; there were produced 1·611 gram of water and 1·965 gram of CO_2. From these data the composition of the gas is thus calculated:—

$$\text{Weight of 1000 c.c.} = 0{\cdot}0896 \times 7{\cdot}98 \text{ (density)} = 0{\cdot}715 \text{ gram.}$$

$$\text{Weight of carbon} = \frac{1{\cdot}965 \times 12}{44} = 0{\cdot}536 \text{ gram.}$$

$$\text{Weight of hydrogen} = \frac{1{\cdot}611 \times 18}{2} = 0{\cdot}179 \text{ gram.}$$

From these numbers the percentage composition may be calculated in the manner already explained.

The simplest possible formula may be determined thus:—

$$\left.\begin{array}{l} \dfrac{0{\cdot}536}{12} = 0{\cdot}044 \\[2ex] \dfrac{0{\cdot}179}{1} = 0{\cdot}179 \end{array}\right\} \text{Numbers in ratio of the number of atoms of carbon and hydrogen.}$$

$$\left.\begin{array}{l} \dfrac{0{\cdot}044}{0{\cdot}044} = 1 \text{ of C} \\[2ex] \dfrac{0{\cdot}179}{0{\cdot}44} = 4 \text{ of H} \end{array}\right\} \text{Lowest number of atoms of C and H in the molecule.}$$

The simplest possible formula of marsh gas must be, from this experiment, CH_4. Whether or not this is the true mole-

cular formula may be determined by calculating the density from the formula, CH_4.

$$\text{Density} = \frac{\text{molecular weight} = C, 12 + H_4, 4 = 16}{2} = 8.$$

This number agrees with the density as determined by experiment; and therefore CH_4 is the correct molecular formula.

Acetylene.—Formula, C_2H_2. Molecular weight, 25·94. Density, 12·97. Specific gravity, 0·896.

152. **Occurrence.**—Acetylene is produced during the combustion of many hydro-carbons in a limited supply of air. Thus, when a Bunsen burner lights at the bottom of the tube, acetylene is produced in considerable quantity.

153. **Preparation.**—By the direct union of carbon and hydrogen at a high temperature acetylene may be formed. The most convenient method of thus preparing the gas is by passing a current of electricity, from a powerful voltaic battery, through two electrodes of carbon enclosed in a glass flask containing hydrogen.

154. **Properties.**—Acetylene is a gas possessing a peculiar and disagreeable odour; it is a non-supporter of combustion, and burns with a bright and luminous flame.

155. **Composition.**—The composition, both by volume and by weight, of this gas may be ascertained in precisely the same manner as that of marsh gas. Acetylene consists of two volumes of carbon combined in the molecule with two of hydrogen, and therefore has the formula C_2H_2.

Ethylene, Ethene, Olefiant Gas, or Heavy Carburetted Hydrogen.—Formula, C_2H_4. Molecular weight, 23·94. Density, 13·97. Specific gravity, 0·965.

156. **Occurrence.**—This gas is one of the most important constituents of coal-gas, being formed when the coal is subjected to destructive distillation.

157. **Preparation.**—Ethylene is most readily prepared by

the action of concentrated sulphuric acid on alcohol, when the acid abstracts the elements of water from the alcohol.

$$\underset{\text{Alcohol.}}{C_2H_5HO} = \underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Water.}}{H_2O.}$$

For this purpose a mixture of one part of alcohol with five parts of concentrated sulphuric acid is gently heated in a large glass flask. Ethylene is readily evolved and may be collected in jars over water.

158. Properties.—Ethylene burns readily with a bright luminous flame, evolving at the same time considerable quantities of smoke. The gas, on being mixed with air or oxygen, explodes violently.

Ethylene combines directly with chlorine to form an oily liquid of the composition $C_2H_4Cl_2$.

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Ethylene dichloride.}}{C_2H_4Cl_2.}$$

159. Composition.—The composition by volume of ethylene is determined by exploding the gas with excess of oxygen in a eudiometer. Thus, if ten volumes of ethylene be taken and forty volumes of oxygen added, there will be found after explosion, the temperature being maintained above 100° C., fifty volumes of gas; that is to say, the volume remains unaltered. On cooling, the volume contracts to thirty, showing that twenty volumes of water gas have been produced. The addition of caustic potash causes an absorption of twenty volumes, showing that that amount of carbon dioxide has been formed. The residual ten volumes of gas are found on testing to be oxygen. Two volumes, therefore, of ethylene produce on combustion two volumes of carbon dioxide and two volumes of water. Applying, as in the case of marsh gas, Avogadro's law, one molecule of ethylene yields two molecules of carbon dioxide and two molecules of water; therefore the molecule of ethylene must contain two atoms of carbon and four of hydrogen, and its formula must be C_2H_4.

By passing a known volume of ethylene over red-hot copper oxide, and collecting and weighing the resultant water and carbon dioxide, the composition by weight may be determined.

Thus 1000 c.c. at N.T.P., having been thus treated, there will have been formed 1·609 gram of water and 3·934 gram of carbon dioxide.

Weight of 1000 c.c. $= 0·0896 \times 13·97$ (density) $= 1·2517$ gram.

$$\text{Weight of carbon} = \frac{3·934 \times 12}{44} = 1·0729 \text{ gram.}$$

$$\text{Weight of hydrogen} = \frac{1·6092 \times 18}{2} = 0·1788 \text{ gram.}$$

The percentage composition may be readily calculated from these numbers.

The simplest formula may be thus deduced :—

$$\left.\begin{array}{l} \frac{1·0729}{12} = 0·0894 \\ \frac{0·1788}{1} = 0·1788 \end{array}\right\} \text{Numbers in ratio of the number of atoms of carbon and hydrogen.}$$

$$\left.\begin{array}{l} \frac{0·0894}{0·0894} = 1 \text{ of C} \\ \frac{0·1788}{0·0894} + 2 \text{ of H} \end{array}\right\} \text{Lowest number of atoms of C and H in the molecule.}$$

The simplest possible formula is therefore CH_2. Whether or not this is the true molecular formula may be determined by calculating the density according to this formula :—

$$\text{Density} = \frac{\text{molecular weight} = \text{C}, 12 + \text{H}_2, 2 = 14}{2} = 7.$$

But the density as determined by direct experiment is 14; therefore the molecular formula must be just double CH_2, that is to say, the molecule is represented by C_2H_4.

160. Combustion of Marsh Gas, Acetylene, and Ethylene.—The combustion of these three bodies affords some interesting examples of the laws of combination by volume. Subjoined are the molecular equations representing the reactions which occur, together with those of some other examples of combustion already familiar to the student.

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Marsh gas. One volume. Two volumes. One volume. Two volumes.

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O.$$

Acetylene. Two volumes. Five volumes. Four volumes. Two volumes.

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

Ethylene. One volume. Three volumes. Two volumes. Two volumes.

$$C + O_2 = CO_2.$$

Carbon. One volume. One vo'ume.

$$2CO + O_2 = 2CO_2.$$

Carbon monoxide. Two volumes. One volume. Two volumes.

$$2H_2 + O_2 = 2H_2O.$$

Hydrogen. Two volumes. One volume. Two volumes.

$$H_2 + Cl_2 = 2HCl.$$

Hydrogen. One volume. One volume. Two volumes.

These equations show very clearly the relation which exists between the volumes of gases and the respective volumes of oxygen required for their combustion. They afford additional illustrations of the method of deducing these quantities from the molecular equations. **As gaseous molecules are assumed** (at the same temperature and pressure) **to occupy the same space, it follows that the number of molecules of any gas participating in a chemical change represents the number of volumes of the gas concerned.**

161. Nature of Combustion.—Everyone is familiar with the general idea of combustion as an act of burning. We may now inquire a little more closely into what is understood by this term. It has already been incidentally remarked that heat is produced when combination occurs between two substances; for instance, the addition of water to sulphuric acid causes a considerable elevation of temperature, because the water and acid unite with each other. There are many other cases in which the heat evolved is much more intense, as, for example, when phosphorus combines with oxygen. **Whenever the heat caused by chemical union is sufficiently intense**

to raise the resultant substances to a temperature at which they emit light, the act of union is termed 'combustion.' The term has gradually come to receive a somewhat wider application; thus certain processes of decay, and also the chemical changes which produce animal heat, are cases of combination with oxygen. Such chemical actions are frequently termed instances of 'slow' combustion.

162. Inflammable Bodies and Supporters of Combustion.—The substances participating in the act of combustion are classified into inflammable bodies on the one hand, and supporters of combustion on the other. Thus, when hydrogen burns in oxygen, the hydrogen is said to be inflammable, and the oxygen a supporter of combustion. **The terms 'combustible' and 'supporter of combustion' are, however, purely relative.** We happen to live in an atmosphere of which oxygen is the active ingredient; when a jet of hydrogen is burned, what takes place is that at the orifice of the jet the hydrogen and the oxygen come in contact and combination ensues. If the atmosphere consisted of hydrogen, then that element would be classified as a supporter of combustion, and oxygen and similar bodies would be inflammable substances. Experiment readily demonstrates that oxygen burns in an atmosphere of hydrogen. Thus, if a large glass globe, such as is used for the combustion of phosphorus in oxygen, be filled with hydrogen gas, and arranged mouth downwards, a jet of oxygen may be burned within it. For this purpose a bladder, or small gas-bag, of oxygen must have attached to it, by means of india-rubber tubing, a piece of glass tube drawn out into a jet. This bag must be weighted so that a gentle stream of oxygen issues. The hydrogen must then be lighted at the mouth of the globe, and the jet of oxygen steadily introduced. The oxygen will be ignited at the flame of the burning hydrogen, and as it is pushed up into the globe will continue to burn, showing clearly that oxygen burns in an atmosphere of hydrogen. The same experiment may be performed with coal-gas and air.

It is seen, therefore, that, for combustion to occur, contact

of the two substances is necessary. It is a matter of indifference which of the two envelops the other. But oxygen being so widely distributed, and the essential constituent of the atmosphere, it and like bodies are classified as supporters of combustion; while hydrogen and bodies of similar character are termed inflammable.

163. Explosion.—When two substances, the one inflammable and the other a supporter of combustion, are intimately mixed with each other, on ignition combination occurs with extreme rapidity. The heat developed enormously increases the pressure of the gases produced as a result of the chemical action, and these give the surrounding air such a severe shock as to cause a loud detonation. **Extremely rapid combustion, attended with more or less noise, is termed explosion.** The mixture which thus explodes is termed an explosive body. If explosive mixtures be confined and then exploded, the resultant pressure may shatter the containing vessel. The explosive force of gunpowder is thus utilised for destroying large masses of rock. A hole is bored in the rock, filled with the powder, and then ignited, with the result of shattering the rock into fragments. The great pressure exerted by exploding gunpowder is employed in guns for the purpose of propelling the bullet. Another interesting example of explosive force being utilised is that of the gas engine, in the cylinder of which a mixture of gas and air is caused to explode. The piston is driven forward by the force of the explosion.

164. Heat of Combustion.—Not only do substances in burning give out heat, but **the amount of heat evolved by the combustion (combination with oxygen) of a given weight of any substance is always the same.** Thus, whether the substance be burned slowly or rapidly, provided it is burned to the same products of combustion, the total amount of heat generated never varies. The following table gives the number of heat-units evolved by the combustion respectively in oxygen and chlorine of one gram of each substance. The student is reminded that a heat-unit is the quantity of heat necessary to arise one gram of water from 0° to 1° C.

HEAT DEVELOPED DURING COMBUSTION.

Substances	In oxygen. Heat-units	In chlorine. Heat-units
Hydrogen . . .	34,462	24,087
Carbon	8,080	
Sulphur	2,220	
Phosphorus . . .	5,747	3,422 (?)
Carbon monoxide . .	2,634	
Marsh gas . . .	13,063	
Olefiant gas . . .	11,942	
Alcohol	6,909	

Of these bodies hydrogen develops by far the greatest amount of heat on combustion, the next place being taken by carbon. Of the various compounds of carbon it will be observed that carbon monoxide, during its further combustion to the dioxide, evolves a considerable quantity of heat. It will be of interest to compare the amount of heat evolved in the two stages of oxidation of carbon. As carbon monoxide contains, according to its formula, but $\frac{12}{28}$ of its weight of carbon, it is evident that one gram of carbon would yield $\frac{28}{12}$ gram of carbon monoxide, and consequently, that one gram of carbon as monoxide would, in its further oxidation to carbon dioxide, evolve

$$\frac{2634 \times 28}{12} = 6146 \text{ heat-units.}$$

But the total number of heat-units evolved by the complete combustion of carbon is only 8080. Therefore one gram of carbon evolves in oxidation to the monoxide

$$8080 - 6146 = 1934 \text{ heat-units,}$$

and during further oxidation to the dioxide, 6146 heat-units. The student is already aware that when the carbon dioxide formed in a fire of carbon passes upwards through red-hot carbon, it is reduced to the monoxide, which in its turn burns on the upper surface of the fire, where there is free access to air. Whenever carbon is burned with a limited supply of oxygen, as where a draught of air is drawn through a furnace containing large quantities of coke or other form of carbon,

the monoxide is the chief product of combustion. This cannot burn until it reaches the air, and accordingly in the older forms of furnace used in metallurgical operations, particularly the blast furnace used for the smelting of iron ores, enormous quantities of carbon monoxide were formed and allowed to burn to waste on the tops of the furnaces. The value of this gas as a fuel is now recognised, and it is consequently drawn off from the upper part of the furnaces and utilised for heating purposes.

165. Temperature of Combustion.—Although the absolute amount of heat produced by the combustion of a unit weight of hydrogen, for example, is always the same, yet the temperature produced may vary within wide limits. Thus, first of all, if within a given space, hydrogen is caused to burn in one instance at twice the rate of another, it follows that, as a greater number of units of heat are evolved in the same period of time, the temperature of that space will be raised proportionately higher. There are other causes which influence the temperature produced by combustion; for example, a jet of hydrogen, which burns the same number of cubic feet per hour, produces flame of much higher temperature when it burns in oxygen than it does when burning in air. If 2 grams of hydrogen are burned in oxygen, the heat evolved has to raise the temperature of the 18 grams of water produced. But if the oxygen is obtained from air, then not only have there to be heated the 16 grams of oxygen, but also the 53·5 grams of nitrogen with which it is mixed. The same number of units of heat are in the one case spread over 18 grams; in the other over $18 + 53·5 = 71·5$ grams of gaseous matter; it follows that the temperature in the first instance must be very much higher than in the second.

166. Luminosity of Flame.—The student will probably think it strange that, although the temperature of the flame of hydrogen burning in oxygen is the highest due to combustion, yet the flame is almost absolutely devoid of luminosity. The reason is that gases—and especially those of low density—radiate very little light even when intensely hot, while solids at

a much lower temperature emit light most abundantly. This is strikingly illustrated by inserting some solid substance in the oxyhydrogen flame; if the flame from the oxyhydrogen blowpipe is caused to impinge on a piece of lime, the light emitted is one of the most intense known, and constitutes the well-known lime-light. It is here the solid substance which radiates so much light, although its temperature must be lower than that of the oxyhydrogen flame by which it is heated.

The various inflammable hydrocarbons burn with different degrees of luminosity; marsh gas and alcohol emit but very little light; olefiant gas, on the other hand, burns with a very luminous and smoky flame. As a general rule, the heavier hydrocarbons produce more light in burning than those which are less dense. During the combustion of such a body as olefiant gas, the hydrogen, being more inflammable, seizes first hold of the oxygen, and more or less of the carbon is liberated either in the free state or else as vapour of exceedingly dense hydrocarbons. The finely divided particles of carbon or dense hydrocarbons, as the case may be, are heated by the burning hydrogen and by abundantly emitting light impart luminosity to the flame.

167. Structure of Flame.—The actual structure of a flame may be studied by observing a jet of coal gas burning from the end of a round pipe, such as at A in fig. 40. In the interior of the flame there is a jet of unburnt gas, marked *a*, *a* in the figure, and appearing black by contrast with the surrounding brighter portions of the flame by which it is enveloped. This bright or luminous zone, *f*, *e*, *g*, is that portion of the flame in which combustion of the hydrogen is proceeding, the unburnt carbon being thereby heated to the point at which it emits light. In such a burner as is figured, there will be seen ascending from the upper portion of this zone a stream of smoke, consisting of carbon, which altogether escapes combustion. Outside *f*, *e*, *g* there may be distinguished another envelope, *b*, *c*, *d*, scarcely at all luminous, and much resembling the flame of

FIG. 40.

burning hydrogen. This outer zone is that in which there is an ample supply of atmospheric oxygen, and consequently complete combustion: this is the hottest part of the flame, although the absence of solid particles causes it to be almost non-luminous.

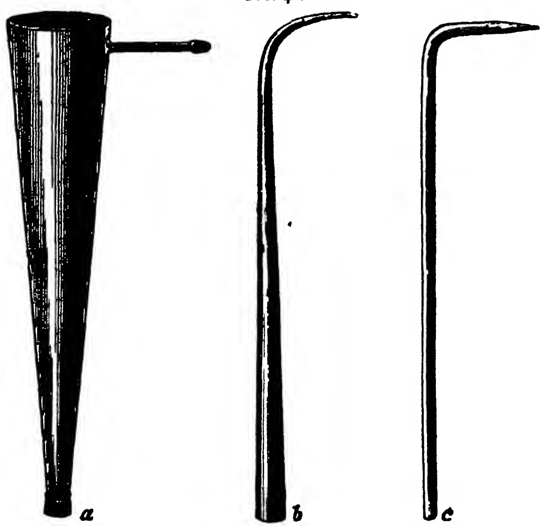
The same divisions of the flame occur in a candle; only in that case the dark interior portion consists of the solid matters of the candle, first melted, then drawn up into the heart of the flame by the capillary attraction of the wick, and finally vaporised by the heat of the flame.

168. Bunsen's Gas-burner.—When a gas flame is required for heating purposes only, it is desirable to attain the most perfect combustion possible. This end is accomplished by causing an admixture of air with the gas before it is burned. The gas-burner invented by Bunsen is familiar to every chemical student. Examination shows that at the bottom of the upright tube are two or more holes communicating with the air; on unscrewing this tube a small jet is seen within, from which the gas emerges. The air-holes may be wholly or partly closed by turning a ring which is fixed around them. If these holes be closed, the gas issues from the top of the burner in a comparatively slow current, and, on being lighted, burns with a luminous and smoky flame. If used for heating purposes, the flask or other vessel heated is soon coated with soot. On opening the air-holes the flame becomes almost non-luminous, and from its appearance is seen to consist of a much more rapidly issuing current of gas. The coal gas emerges at the same rate, but carries with it a considerable volume of air, which has entered through the air-holes. This flame is smokeless, and heats a flask more rapidly than would the luminous flame from the same burner.

169. Blowpipe Flame.—The effect of converting a luminous flame into one devoid of light, but possessing considerable heating powers, is also obtained by blowing a current of air from a jet into the flame. The instrument employed for this purpose is termed a blowpipe, and is constructed in several forms, two of which are shown in fig. 41, *b* and *c*; but for

laboratory use the conical form devised by Black is the most convenient; it is represented in fig. 41, *a*. The conical tube is preferably of brass, and has a bone or ivory mouthpiece at the smaller end; the other is closed, and near it, through the

Fig. 41.



side of the tube, a smaller one projects, to the end of which the jet is attached. The moisture of the mouth collects, while blowing, in the end of the cone instead of being blown out through the jet. In using a blowpipe the air must be forced out by the cheeks, and *not* from the lungs.

A blowpipe may be used with either a spirit or oil lamp, but in all cases where gas is obtainable it will be found most convenient. A suitable form of flame is obtained by the use of a jet to be dropped inside the tube of a Bunsen burner, or a tube with the same shaped orifice is sometimes made to screw on to the base of the bunsen (as in fig. 42), instead of the ordinary brass tube, which is first unscrewed. With a tube of this kind the ring must be turned so as to shut off the air at the bottom of the burner.

There are two varieties of blowpipe flame, known respectively as the '**reducing**' and '**oxidising**' flames, from their action on oxides and metals. The reducing flame is shown in fig. 42. To produce it, the jet of the blowpipe must be held just outside the flame, and the instrument blown through gently; the flame should appear of a luminous yellow tinge, through its still containing unoxidised carbon. This exerts a powerful reducing action, the carbon combining with the oxygen of many oxides when placed in it. An 'oxidising' flame (fig. 43) is produced by placing the blowpipe jet within the flame, and blowing rather harder. The flame should be sharply defined. The point of the fine blue cone in the middle of the flame is the region of greatest heat. Slightly beyond this there is an excess of air, and this readily yields oxygen to any substance capable of combining with it. The oxyhydrogen blowpipe is a modification of the ordinary instrument, in which a stream of oxygen is employed instead of ordinary air, hydrogen being taken as the fuel instead of coal-gas. This instrument has already been described in Chapter III., in which an illustration of the oxyhydrogen blowpipe (fig. 11) is also given. By means of this blowpipe, platinum and other most refractory substances may be reduced to the liquid state.

FIG. 42.

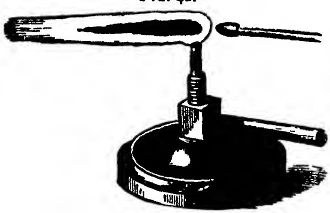
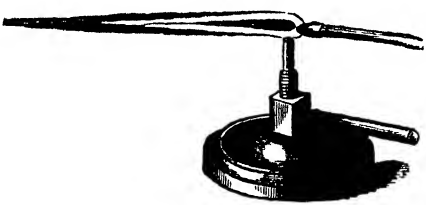


FIG. 43.



170. Lamp Chimneys.—The effect of the lamp chimney of a petroleum or Argand gas-lamp is apparently just the opposite of that produced by the Bunsen burner. If either of these be lighted, it burns with a dull, smoky flame, but on

fixing the chimney the flame becomes smokeless and much more luminous. The first result of the action of the chimney is to draw a current of air up around the flame (in the case of the Argand through the interior as well as the exterior). That this produces greater brightness is, at first sight, contradictory to what has already been seen of the effects of air in the Bunsen burner. But with the lamp-chimney the air is drawn up, not into the flame, but surrounding it; the effect of this is more complete and intense combustion in the outside zone of the flame; consequently the luminous envelope is heated more intensely and emits more light. The brisker current of air causes also the complete consumption of the smoke. If the current of air be too rapid, the brightness of the flame is thereby diminished, for with excess of air the envelope of complete combustion is unduly enlarged at the expense of that of luminosity; the flame, in fact, partakes more or less of the character of that of the bunsen. That in some cases the chimney causes too great a draught may be readily seen by partly closing the top, by placing on it a small piece of tin-plate. This lessens the draught, and very frequently causes the flame to increase in size and emit more light.

171. Chlorides of Carbon.—Chlorine and carbon cannot be made to directly combine; in fact, as already stated, charcoal is purified from traces of hydrogen by passing chlorine over the charcoal when red-hot. Hydrochloric acid is formed, but the carbon is unaltered. By acting on marsh gas with chlorine, it is possible to displace successive atoms of hydrogen by chlorine, until finally carbon tetrachloride, CCl_4, is produced. This change takes place on exposing a mixture of the two gases to direct sunlight. Carbon tetrachloride is also formed when a mixture of chlorine and carbon disulphide vapour is passed through a red-hot tube—

$$\underset{\text{Carbon disulphide.}}{CS_2} + \underset{\text{Chlorine.}}{8Cl_2} = \underset{\text{Carbon tetrachloride.}}{CCl_4} + \underset{\text{Sulphur chloride.}}{S_2Cl_2}$$

The two are separated by the action of sodium hydrate, which decomposes the sulphur chloride. Carbon tetrachloride is a very stable compound, and is a colourless liquid, sp. gr. 1·6,

boiling-point, 77° C. It possesses a pleasant ethereal odour, and behaves somewhat like chloroform, $CHCl_3$, which is one of the intermediate products of the chlorination of marsh gas. While the tetrachloride corresponds with marsh gas, there is another chloride, C_2Cl_4, corresponding to ethylene, C_2H_4. A third chloride is carbon hexachloride, C_2Cl_6. These chlorides, although distinctly inorganic, are so closely related to organic bodies, that their fuller investigation is usually treated as a section of organic chemistry.

CHAPTER XIII

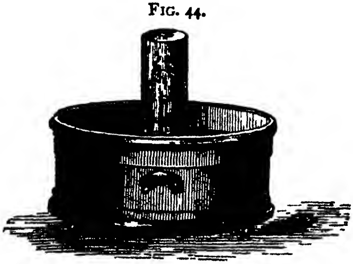
NITROGEN AND THE ATMOSPHERE

Nitrogen.—Symbol, N. Atomic weight, 14·01. Density, 14·01. Specific gravity, 0·971. Molecular weight, 28·02.

172. **Occurrence.**—Nitrogen exists in the free state in the atmosphere, in combination with oxygen and metals in certain native nitrates, and also is an essential constituent of many organic compounds.

173. **Preparation.**—There are several methods of preparing this gas, based on the removal of oxygen from the air by bodies having an affinity for that element; but in order that nitrogen only shall remain, it is necessary that the substance used be such that the resulting body can be easily separated from the gas. Phosphorus is very convenient for this purpose, as the solid pentoxide produced by its combustion is very soluble in water. An upright deflagrating spoon containing the phosphorus is

FIG. 44.



placed in a pneumatic trough partly filled with water (fig. 44). The phosphorus is lighted, and at once a gas jar inverted over it. The combustion being over and the gas once more cooled to the ordinary temperature, it is found that about four-fifths of the original volume remain. This residual gas is nitrogen.

A more accurate measurement may be made by removing the oxygen by the slow oxidation of phosphorus which goes on at ordinary temperatures. For this purpose the same apparatus may be used, a piece of phosphorus being taken which is sufficiently large to prevent its being submerged in the liquid which accumulates in the spoon, owing to the deliquescence of the oxide of phosphorus.

The oxygen may also be removed by the action of metallic copper. If an iron tube be filled with copper turnings and made red-hot in a furnace, the copper immediately combines with the oxygen of any air which may be passed through, leaving the nitrogen—

$$\underset{\text{Copper.}}{2Cu} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Copper oxide.}}{2CuO.}$$

Iron likewise removes the oxygen from air, especially if it be caused to oxidise more readily by the addition of some ammonium chloride.

There are several other methods of preparing nitrogen which are interesting from a theoretical point of view. For instance, the gas is evolved by passing chlorine into an excess of ammonia. The hydrogen and chlorine unite, and nitrogen is liberated.

$$\underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Hydrochloric acid.}}{6HCl} + \underset{\text{Nitrogen.}}{N_2.}$$

A secondary reaction goes on between the acid formed and the excess of ammonia; thus—

$$\underset{\text{Ammonia.}}{6NH_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Ammonium chloride.}}{6NH_4Cl.}$$

The two equations may be grouped into one; thus—

$$\underset{\text{Chlorine.}}{3Cl_2} + \underset{\text{Ammonia.}}{8NH_3} = \underset{\text{Ammonium chloride.}}{6NH_4Cl} + \underset{\text{Nitrogen.}}{N_2.}$$

In preparing nitrogen by this method care must be taken to have the ammonia largely in excess, as otherwise an explosive compound (chloride of nitrogen) may be formed.

Another interesting method of preparing nitrogen is by the action of heat on the salt known as ammonium nitrite. This contains oxygen and hydrogen in the proportions necessary to form water: they combine and nitrogen is liberated.

$$\underset{\text{Ammonium nitrite.}}{NH_4NO_2} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen.}}{N_2}.$$

It is usual to prepare the ammonium nitrite at the time of the experiment, that body being somewhat unstable. Ammonium chloride being added to potassium nitrite, the following decomposition takes place:—

$$\underset{\text{Potassium nitrite.}}{KNO_2} + \underset{\text{Ammonium chloride.}}{NH_4Cl} = \underset{\text{Ammonium nitrite.}}{NH_4NO_2} + \underset{\text{Potassium chloride.}}{KCl}.$$

For ordinary purposes of experiment this last mode of preparation is a convenient one to employ in order to obtain nitrogen.

174. **Properties.**—Nitrogen differs remarkably in properties from oxygen, with which it is associated in the atmosphere. The one is specially characterised by its great chemical activity; the other is most inactive. It is a colourless, odourless, neutral, and tasteless gas, which is neither inflammable nor a supporter of combustion. It is not poisonous, but is unable to support life. Animals placed in it speedily die through suffocation. By the action of intense heat it may be caused to combine with oxygen, to form a ruddy-coloured gas, nitrogen peroxide, NO_2, which, by uniting with more oxygen and water, produces nitric acid. Small quantities of nitric acid are thus produced in the atmosphere by lightning discharges. The effect may be imitated on the small scale by passing a series of sparks from an induction coil through moist air contained in a small glass globe. The air assumes a faint red tint, and litmus paper placed in the globe shows that it possesses an acid reaction.

Nitrogen is but slightly soluble in water: 100 volumes at 0° C. dissolve but 1·48 volumes of this gas.

The Atmosphere.—A gaseous mixture. Density, 14·47. Specific gravity, 1·00.

175. **Occurrence.**—This gaseous body, which envelops the earth, is of vast importance to us who live and breathe in it. Its existence is demonstrated whenever it is set in rapid motion, as we then have winds; and these, when sufficiently violent, produce well-known and striking physical effects. That air, among the other properties of matter, possesses weight is capable of easy demonstration by experiment; for on weighing a strong flask fitted with a stopcock, and then exhausting it by means of an air-pump and reweighing, it is found to have become considerably lighter. The barometer shows that air possesses the property of causing pressure.

176. **Composition.**—The composition of the atmosphere has been made the subject of many careful experiments, which show it to be a mixture of nitrogen and oxygen approximately in the proportion of four to one. A rough kind of analysis of air is made on the oxygen being removed by phosphorus. In addition to these two elements there are also present varying quantities of aqueous vapour—carbon dioxide, ammonia, nitric acid, and traces of other bodies. Its average composition is shown in the following table:—

	Oxygen	20·61
	Nitrogen	77·95
	Carbon dioxide	0·04
	Aqueous vapour	1·40
	Nitric acid	traces.
	Ammonia	traces.
	Carburetted hydrogen	traces.
In towns	Sulphuretted hydrogen	"
In towns	Sulphur dioxide	"

The proportion of nitrogen to oxygen in air is remarkably constant, but little variation from the above being found in air collected in the most varied localities; still slight but marked differences are observed in samples collected from different sources. The results of careful analyses of air, freed from carbon dioxide and aqueous vapour, give the following average composition:—

	By measure.	By weight.
Nitrogen	79·19	76·99
Oxygen	20·81	23·01
	100·00	100·00

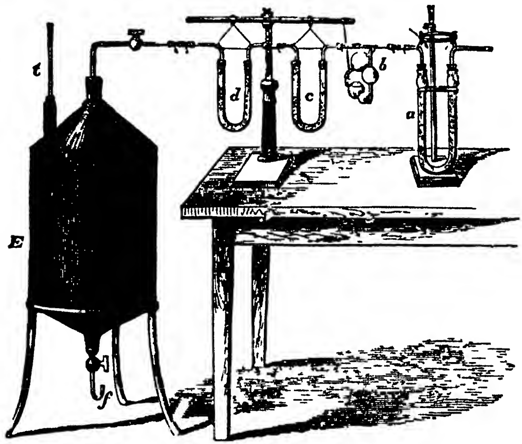
The composition by volume may be determined by using a eudiometer tube similar to that employed for showing the production of water by the union of oxygen and hydrogen. A measured quantity of air, freed from moisture and carbon dioxide, is placed in the eudiometer, and hydrogen added in excess of that necessary to combine with the whole of the oxygen present; on the passage of a spark, union of the hydrogen and oxygen is affected, and on the gas regaining its original temperature the volume is found to be much less. As water is composed of two volumes of hydrogen to one of oxygen, the amount of oxygen present in the gaseous mixture is one-third of the diminution observed. The eudiometer employed for this purpose should be graduated. Supposing that 10 c.c. of air have been introduced and 5 c.c. of hydrogen added, after the explosion the volume will be found to be reduced from 15 to about 9 c.c.; 10 c.c. of air therefore contain approximately $\frac{6}{3} = 2$ c.c. of oxygen, the more accurate figures being those given above.

The composition by weight is ascertained by passing air over red-hot copper, due precautions being taken to avoid error. The copper is placed in a piece of difficultly-fusible glass tubing, with which it is weighed; an exhausted receiver, is also weighed, and attached to one end of this tube; the other is connected with U-tubes filled with caustic potash and sulphuric acid respectively, for the purpose of removing carbon dioxide and water. The glass tubing is raised to red heat, the stop-cock of the receiver is opened, and a slow current of air passes over the copper; its oxygen is removed and nitrogen only passes into the empty receiver. The gain in weight of the copper represents the weight of oxygen, and that of the receiver the weight of nitrogen.

The proportion of aqueous vapour present in air may be determined by passing a known volume of air through a

weighed tube containing either calcium chloride or pumice moistened with concentrated sulphuric acid. For this purpose the apparatus shown in fig. 45 may be employed, which apparatus serves also for the estimation of carbon dioxide.

FIG. 45.



The vessel E is an aspirator, which may have a capacity of some 50 litres; to it are attached the tubes *d* and *c*, which contain respectively calcium chloride and fragments of ground potassium hydrate. In the bulbs *b* is placed a concentrated solution of potassium hydrate, and the tube *a* contains the calcium chloride. On opening the stopcock *f* at the bottom of the aspirator, the water runs slowly out and draws the same volume of air through the tubes. The moisture is absorbed in *a*, the carbon dioxide in *b*, and possibly traces in *c*. The difference in weight between these tubes and bulbs before and after the passage of the air gives the weight of carbon dioxide and moisture respectively. The tube *d* is interposed in order to prevent any aqueous mixture from finding its way backward from the water contained in E.

Aqueous vapour in air is also capable of determination by a purely physical method. For this purpose the air is cooled until it commences to deposit moisture; the temperature at

which dew thus forms is measured, and as that temperature varies with the proportion of moisture present, such moisture may be thus determined. The greater the quantity of moisture, the higher is the temperature at which dew commences to be deposited. Instruments for the purpose of this determination are styled hygrometers.

For the estimation of carbon dioxide in air a convenient volumetric method is adopted; for this purpose, standard solutions of oxalic acid (acid) and barium hydrate (alkaline) are prepared of such a strength that they exactly neutralise each other. A glass vessel of known capacity, say ten litres, is taken, filled with water, and emptied in the place in which it is desired to collect a sample of air. Having the vessel thus filled with the air to be tested, it is carefully stoppered, and a known quantity of barium hydrate solution quickly run in together with one or two drops of phenolphthalein. The vessel is shaken until the whole of the air is exposed to the action of the barium hydrate. Barium carbonate is formed and the hydrate thus in part neutralised. The oxalic acid is next added from a burette until the red tint of the phenolphthalein disappears. In this way the excess of barium hydrate is measured; the difference between such excess and the quantity originally taken gives the quantity neutralised by the carbon dioxide. The barium hydrate solution is made of such a strength that each c.c. represents a definite quantity of carbon dioxide.

177. **Air a Mixture.**—That air is a mixture and not a compound may be proved in many ways; in the first place the oxygen and nitrogen are not present in any simple multiple of their atomic weights, which is a necessity in all compounds. Air also differs remarkably from those compounds of the two elements with which chemists are acquainted. If a mixture be made of nitrogen and oxygen in the proportion in which they exist in air, no alteration of volume takes place, neither is there any increase of temperature; the mixture exhibits all the properties of air.

The most conclusive evidence of their being mixed, and not combined, is that they may be separated by the action of

water as a solvent. Oxygen is more soluble than nitrogen, and if water, which has been previously freed from gases by boiling be shaken up with air, and then again boiled, the expelled gas is found on analysis to be much richer in oxygen than was the air, the oxygen amounting to about 34 per cent. of the dissolved gases.

It will be interesting here to note the difference between air on the one hand and water on the other. In air the two most important constituents are not present in the same absolutely unvarying proportion. On oxygen and nitrogen being mixed in the same proportions as they exist in air, no alteration in volume occurs, and the mixture exhibits properties which are a mean of those of the two ingredients. Further they may be separated by the action of water as a solvent.

With water the hydrogen and oxygen are always present in absolutely unvarying proportions. When these gases are mixed and a light applied a violent explosion occurs; the water produced condenses to a liquid possessing properties altogether different from those of its constituents. The explanation is that air is a mixture, and water a chemical compound.

178. Functions of Atmospheric Carbon Dioxide.—It has already been pointed out that carbon dioxide is present in air, and that the breathing of animals and the burning of carbonaceous bodies are continually supplying this gas; although this operation is proceeding without intermission, the quantity of carbon dioxide present in the atmosphere remains remarkably constant. Its amount varies between 3 and 6 parts in 10,000, according to the locality where, and time when, the gas is collected. This quantity, though small, is of vast importance to the vegetable kingdom, as it is the source from which all organic carbon is derived in nature. Animals can only assimilate carbon from previously existing organic compounds. Vegetables decompose carbon dioxide, using the carbon in the formation of their tissues, and liberating the oxygen in the free state.

The effects, therefore, of animal and vegetable life on the atmosphere are opposite in character: the one removes oxygen

and returns carbon dioxide, the other decomposes this compound, and again yields oxygen to the air (this return action is, however, partially balanced by the ordinary progress of decay); these two processes going on simultaneously keep the proportion of carbon dioxide in air within constant limits. The decomposition of certain rock-forming minerals, as felspar, by the action of the carbon dioxide of the atmosphere, which combines with the bases that they contain, is another important drain on the amount of that gas present in air.

179. **Other Constituents.**—The amount of aqueous vapour which the atmosphere contains varies considerably; but it is always present in more or less quantity. Its presence may be demonstrated by bringing a vessel of ice cold water into a room: the aqueous vapour condenses on the outside as a film of moisture.

Ammonia is only found in air in minute traces. These, however, are important, as from them plants obtain a great proportion of their nitrogen.

CHAPTER XIV

AMMONIA

Formula, NH_3. Molecular weight, 17·01. Density, 8·5. Specific gravity, 0·59. Melting-point, −75° C. Boiling-point, −38·5° C.

180. **Occurrence.**—This, the only compound of nitrogen and hydrogen known in the free state, exists in small quantities in the atmosphere, and also in rain-water. It is probably a resultant product of the oxidation of different organic substances in the presence of moist air. The oxygen of the water acts as the oxidising agent, and the nascent hydrogen combines with nitrogen to form small quantities of ammonia. It is produced in considerable quantity in the decomposition of animal and vegetable bodies which contain nitrogen. The urine and

excreta of animals contain refuse nitrogenous matter. This after a time becomes changed into ammonia, and thus causes these substances to be such valuable manures, as plants are incapable of assimilating nitrogen while free, but are able to do so when that element is presented to them as ammonia.

181. Preparation.—Nitrogen and hydrogen do not unite readily, but may be caused to do so by passing a silent electric discharge from an induction coil through a mixture of the two gases. It is not possible in this way to cause the union of the whole of the nitrogen and hydrogen present unless the ammonia is removed as rapidly as formed, because as soon as about 3 per cent. of ammonia is present the electric discharge once more causes its decomposition into free nitrogen and hydrogen. The ammonia may be removed in this experiment by causing the reaction to take place over a solution of hydrochloric acid, which combines with the ammonia to form ammonium chloride. Conversely if this experiment be commenced with pure ammonia, decomposition into nitrogen and hydrogen gases proceeds until only about three per cent. of ammonia remains.

In the presence of favourable deoxidising agents nitric acid and nitrates are reduced to ammonia. Thus if zinc be added to dilute nitric acid, the following reaction occurs :—

$$\underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Nascent hydrogen.}}{8H} = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{3H_2O.}$$

Similarly, nitrates are reduced to ammonia on being treated with a solution of pure potassium hydrate, to which metallic aluminium foil is added. The first stage of the reaction is the formation of potassium aluminate and nascent hydrogen which attacks the nitric acid :—

$$\underset{\text{Potassium hydrate.}}{24KHO} + \underset{\text{Aluminium.}}{8Al} = \underset{\text{Potassium aluminate.}}{4(K_2O)_3Al_2O_3} + \underset{\text{Nascent hydrogen.}}{24H.}$$

$$24H + 3HNO_3 = 3NH_3 + 3H_2O.$$

Small quantities of nitrates may be quantitatively determined by their reduction in this manner to ammonia, which is subsequently estimated.

On heating nitrogenous organic substances such as horn,

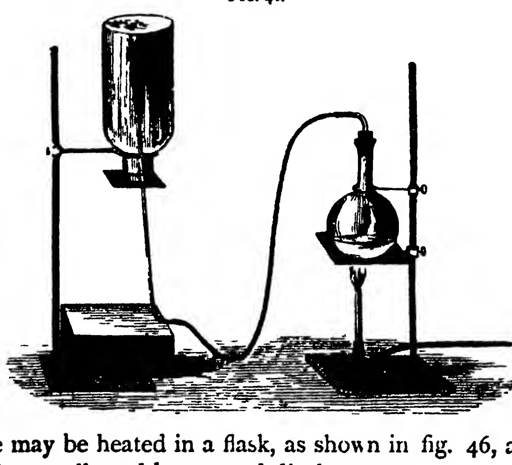
hair, the white of egg or gluten of wheat, in a closed vessel, they are decomposed, and a portion of the nitrogen is evolved as ammonia. If the organic matter be first mixed with an excess of sodium or potassium hydrate, the whole of the nitrogen is evolved in this form; this reaction serves as a method for the estimation of nitrogen in organic bodies.

Ammonia may be prepared from any of the ammoniacal salts by heating with a stronger base, as lime or soda. Of these lime is preferred because of its cheapness. If ammonium chloride and lime be heated together, the following reaction takes place:—

$$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Quicklime.}}{CaO} = \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Ammonia.}}{2NH_3.}$$

Both the ammonium chloride and the quicklime should be carefully dried, and then intimately mixed together. The

FIG. 46.



mixture may be heated in a flask, as shown in fig. 46, and the evolved gas collected by upward displacement.

182. Manufacture.—For manufacturing purposes ammonia is always prepared by the destructive distillation of bones, animal refuse, or other nitrogenous organic matter. Thus the heating of bones or other animal refuse to redness in

order to obtain animal charcoal also yields ammonia, which condenses with the watery products of distillation.

Coal contains about 2 per cent. of nitrogen, and in like manner evolves ammonia when heated. As this substance is subjected to destructive distillation on the large scale in the manufacture of coal-gas, it affords a cheap and plentiful source of ammonia. The ammonia passes over with the gas, and is dissolved by the condensed moisture. This constitutes the gas- or ammoniacal-liquor of the works. From this ammoniacal salts are prepared by the addition of acids.

Solution of ammonia is prepared commercially by heating ammoniacal gas liquor with milk of lime; the evolved gas is filtered through tubes containing charcoal, and then passed through a series of Woulffe's bottles filled with water and connected together, so that the gas escaping from each is conducted to the next of the series. Each of these bottles is fitted with a safety tube, by which air enters in case there is a vacuum. The passage of the gas is continued until a saturated solution is obtained.

183. Properties.—Ammonia is a colourless gas with a most pungent and characteristic odour, which is pleasant when the gas is mixed with air; but in the undiluted state the gas acts as a powerful irritant, bringing tears to the eyes, and if accidentally inhaled, even in small quantities, destroys the surface of the mucous membrane of the mouth, and may produce even fatal effects by its action on the lungs. The solution in water has a burning and disagreeable taste. The gas may be condensed to a liquid by a temperature of $-50°$ C., or a pressure of about 7 atmospheres at 15° C. Like other liquefied gases, liquid ammonia is very volatile, producing great cold in evaporating. This property causes it to be largely used in the manufacture of artificial ice. The gas is remarkably soluble in water, which dissolves at 0° C. 1050 times its volume of the gas; at 15° C. 727 volumes. The concentrated solution readily evolves gas on being heated, and may frequently be used with advantage as a source of the gas. At ordinary temperatures the solution gives off gas, hence its pungent odour

The following table gives the strength of solutions of pure ammonia of various densities :—

Density	Ammonia in 100 parts by weight	Density	Ammonia in 100 parts by weight
1·0000	0·0	0·9251	20·0
0·9915	2·0	0·9191	22·0
0·9831	4·0	0·9133	24·0
0·9749	6·0	0·9078	26·0
0·9670	8·0	0·9026	28·0
0·9593	10·0	0·8976	30·0
0·9520	12·0	0·8929	32·0
0·9499	14·0	0·8885	34·0
0·9380	16·0	0·8844	36·0
0·9314	18·0	—	—

Ammonia is one of those gases which are absorbed with exceeding readiness by charcoal; this body, when freshly burned, absorbs about 90 times its own volume of the gas.

Ammonia is a non-supporter of combustion, and non-inflammable at ordinary temperatures; but when gently heated it takes fire and burns with a greenish-yellow flame, water being produced and nitrogen liberated.

$$\underset{\text{Ammonia.}}{4NH_3} + \underset{\text{Oxygen.}}{3O_2} = \underset{\text{Nitrogen.}}{2N_2} + \underset{\text{Water.}}{6H_2O.}$$

In common with potassium and sodium hydrates, ammonia possesses the property of being able to restore the blue colour to reddened litmus. It neutralises the strongest acids, and forms a well-marked and most important series of salts. The composition of some of these is thus shown :—

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ammonium chloride.}}{NH_4Cl.} \quad \bullet \quad \underset{\text{Sodium chloride.}}{NaCl.}$$

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Ammonium nitrate.}}{NH_4NO_3.} \quad \bullet \quad \underset{\text{Sodium nitrate.}}{NaNO_3.}$$

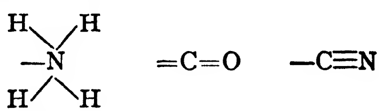
$$\underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4.} \quad \bullet \quad \underset{\text{Sodium sulphate.}}{Na_2SO_4.}$$

The salts of sodium are also written in a separate column, for the sake of comparison. It will be seen that the group NH_4 and sodium occupy corresponding places. Further, this

group may be expelled from one chemical compound and caused to enter another without decomposition.

184. Compound Radicals.—This is only one instance of a group of elements entering into the composition of a body, and performing functions very similar to those of an atom of an element. Such groups are not only found to form numbers of very definite compounds, but may be even transferred from one compound to another without undergoing decomposition. **Groups of atoms of different elements which possess a distinct individuality throughout a series of compounds, and behave therein as though they were elementary bodies, are termed 'compound radicals.'**

The compound radicals are formed by the union of atoms in such a manner as to produce a compound having unsatisfied valency. In addition to the group NH_4, carbon monoxide, CO, and the semi-molecule (CN) of cyanogen, C_2N_2, act as compound radicals. Their unsatisfied valency is shown in the following graphic formula :—



NH_4. CO. CN.

The number of unsatisfied valency links is the measure of the quantivalence of the compound radical. Thus —NH_4 and —CN are monads, while carbon monoxide is a dyad radical. Compound radicals are of extremely frequent occurrence among organic compounds; so strikingly is this the case, that it has been proposed to term organic chemistry 'the Chemistry of the Compound Radicals.'

185. Ammonium and its Salts.—The group NH_4 is one of the best and most striking examples of a compound radical. Because it thus behaves in so many compounds as though it were an element, it has received a name, ***ammonium***, for which the symbol Am is sometimes used. Ammonium chloride is written either NH_4Cl or AmCl. Ammonium,

however, cannot be isolated, but immediately splits up into ammonia and free hydrogen. The solution of ammonia in water is sometimes conveniently represented as a hydrate of ammonium; thus :—

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Ammonium hydrate.}}{NH_4HO.}$$

This, again, is analogous in composition to sodium hydrate, NaHO.

Ammonium hydrate produces in many cases the same chemical reaction as does either sodium or potassium hydrate. Thus all these bodies produce the same precipitate of ferric hydrate, $Fe_2(HO)_6$, from a solution of ferric chloride, Fe_2Cl_6.

By the direct union of gaseous ammonia with acids the salts of ammonium are formed. As in all other cases of direct union, considerable heat is evolved. On bringing together the mouths of two gas-jars, the one containing ammonia, and the other hydrochloric acid, and then removing the plates by which the mouths are covered, the two gases at once combine, forming a dense cloud of ammonium chloride, and at the same time becoming sensibly warm to the hand.

Salts of ammonium with volatile acids may in some cases be sublimed without the production of any permanent chemical change, as with ammonium chloride. Others are decomposed, as ammonium nitrate; those with non-volatile acids, as ammonium phosphates, are decomposed; the acid remains, and free ammonia is evolved.

The ammonium compounds will be treated more fully in the part of this work which deals with the metals.

186. Dissociation.—Although ammonium chloride may be sublimed and recondensed without apparent change, yet that some change occurs is shown by the density of the chloride in the vaporous form. From the formula NH_4Cl the calculated vapour-density is 26·69; but on actual determination the vapour-density is found to be 13·34, or only half that required by the formula. This anomaly is explained by the assumption that ammonium chloride cannot exist in the vaporous condition, but is decomposed into the two molecules

of ammonia and hydrochloric acid, having the densities respectively of 8·5 and 18·18. The density of a mixture of these in equal volumes is 13·34, a figure which agrees with the observed vapour-density of the gas resulting from the heating of ammonium chloride. On the mixed ammonia and hydrochloric acid gases becoming cool, they again unite to form ammonium chloride. Proof of the correctness of this theory is furnished by the fact that the gases can be separated by gaseous diffusion. If the vaporised ammonium chloride be passed through a red-hot porous porcelain tube enclosed within another which is impervious, diffusion proceeds through the walls of the porous tube. This tube arrangement is somewhat similar to that of a Liebig's condenser; as ammonia is considerably the less dense of the two gases, it diffuses through the porcelain tube the more rapidly, and on collecting the gas from the annular chamber between the two tubes, it is found to have an alkaline reaction. On the other hand, the gas which escapes from the end of the porous tube reddens litmus, owing to its containing an excess of hydrochloric acid. **The resolution of molecules, by their subjection to an elevated temperature, into others of a simpler nature is termed 'dissociation.'** As the temperature becomes lower, the more complex molecules are usually again formed, unless the gaseous molecules are separated from each other while too hot to combine together. Compounds may be thus resolved into simpler bodies or elements; and elementary molecules into simpler molecules of the same element.

187. Industrial Applications.—Ammonia is largely used as a reagent in the chemical laboratory. It is also employed in the manufacture of aniline colours and in the preparation of carbonate of soda by what is called the soda process. In the liquid (condensed) form it is largely used in the manufacture of artificial ice. Ammonium salts have also an extended application, to which reference will be made when describing their preparation and properties.

188. Composition of Ammonia.—On passing ammonia

gas through a red-hot porcelain tube charged with copper turnings, the following change occurs :—

$$\underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Nitrogen.}}{N_2} + \underset{\text{Hydrogen.}}{3H_2}.$$

As two molecules of ammonia have produced one molecule of nitrogen and three of hydrogen, the volume will have doubled. On collecting some of the mixed gas in a eudiometer, say eight volumes, and then adding four volumes of oxygen and exploding, there will be a diminution of nine volumes, owing to the formation of water. As when water is formed, two volumes of hydrogen and one volume of oxygen disappear, then in this case six volumes of the gas in the eudiometer must have consisted of hydrogen. If potassium hydrate and pyrogallic acid be next added, there will be a further diminution of one volume, resulting from the absorption of the excess of oxygen. Two volumes of gas will remain, which consist of the nitrogen of the ammonia. We therefore find that the eight volumes of mixed gas consist of six volumes of hydrogen and two of nitrogen.

The composition by weight may be ascertained by passing a measured quantity of dry ammonia over red-hot copper oxide ; water is formed and may be collected by calcium chloride. Nitrogen passes over in the free state. The hydrogen is calculated from the water, and the difference of weight between that and the ammonia represents the nitrogen.

CHAPTER XV

OXIDES AND ACIDS OF NITROGEN

189. Nitrogen Oxides.—There are five compounds of nitrogen and oxygen known, two of which, by union with water, form acids : their names and composition are :—

Nitrogen monoxide, or nitrous oxide, N_2O.
Nitrogen dioxide, or nitric oxide, NO (or N_2O_2).
Nitrogen trioxide, or nitrous anhydride, N_2O_3.

Nitrogen tetroxide, or nitric peroxide, NO_2 (or N_2O_4).
Nitrogen pentoxide, or nitric anhydride, N_2O_5.

By the action of water we have—

$$N_2O_3 + H_2O = 2HNO_2, \text{ Nitrous acid.}$$
$$N_2O_5 + H_2O = 2HNO_3, \text{ Nitric acid.}$$

Nitric acid is by far the most important of these bodies, and, as the whole of the others are prepared from it, nitric acid is conveniently studied first.

Nitric Acid.—Formula, HNO_3. Molecular weight, 62·89. Specific gravity of liquid, 1·53. Melting-point, about −55° C. Boiling-point, 84·5°.

190. **Occurrence.**—Nitric acid is produced in small quantities in the atmosphere, from which it is separated by rain, which therefore usually exhibits traces of this acid when subjected to analysis. The salts of nitric acid with soda and potash (sodium and potassium nitrates) are its most common sources. Layers of potassium nitrate are found incrusting the soil in India and of sodium nitrate in parts of Chili and Peru; the latter of these is the more plentiful. These nitrates are produced by the oxidation of nitrogenous organic matter in the presence of the bases potash or soda. Potassium nitrate is also known as saltpetre or nitre; sodium nitrate is frequently called Chili saltpetre or cubic nitre, from the shape of its crystals.

191. **Preparation.**—Nitric acid is always prepared by the action of sulphuric acid on a nitrate, usually either that of sodium or potassium. The two are mixed in a retort, and on the application of heat nitric acid, being more volatile, distils over, leaving acid sodium sulphate:—

$$\underset{\text{Sodium nitrate.}}{NaNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Acid sodium sulphate.}}{NaHSO_4}.$$

For laboratory purposes the arrangement of retort and receiver shown in fig. 47 may be adopted.

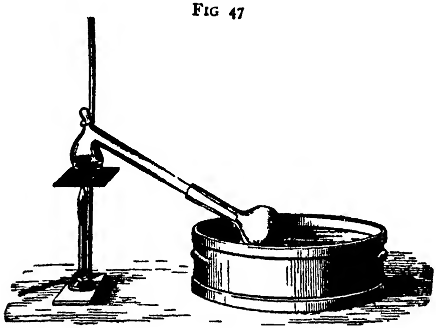
The receiver is kept cool by submersion in the cold water in the pneumatic trough.

On the application of a more intense heat the acid sulphate of sodium is capable of acting on another quantity of the nitrate, with the formation of the normal sulphate :—

$$\underset{\text{Acid sodium sulphate}}{NaHSO_4} + \underset{\text{Sodium nitrate}}{NaNO_3} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Nitric acid}}{HNO_3}.$$

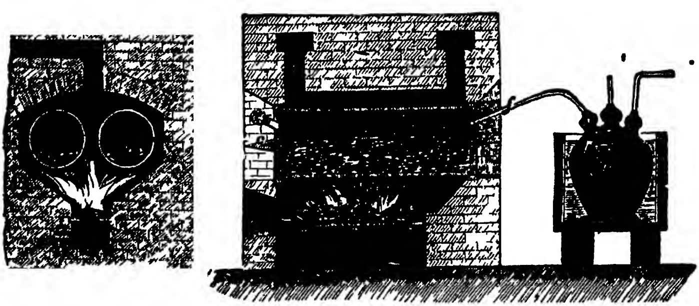
The temperature necessary for this reaction, however, partly decomposes the nitric acid produced.

FIG 47



192. Manufacture—In preparing nitric acid on the large scale the manufacturer avails himself of the second of the reactions just given. Large cast iron retorts, about 6 feet

FIG 48



in length by 3 feet diameter, are employed. These are arranged in pairs in a furnace, as shown in fig 48.

Each retort is fastened by a movable door of flagstone, *c*, at each end, and the upper portion is protected from the acid vapours by a lining of fireclay. The nitrate is added through the opening, *c*, which is then fastened; about half its weight in concentrated sulphuric acid (or the equivalent quantity of weaker acid), is then added through a funnel at *e*, which aperture is then closed by a plug. The nitric acid distils over through the pipe *f*, and is condensed in a series of stoneware bottles, the first of which, *B*, is shown in the figure. At the close of the operations the sodium sulphate is removed from the retort by the opening at *c*. The acid as thus prepared contains, as impurities, the lower oxides of nitrogen, from which it may in great part be freed by re-distillation with an equal volume of sulphuric acid. This distillate being gently warmed, and having a current of dry air passed through it, becomes quite colourless and free from any lower nitrogen oxides.

193. **Properties.**—Nitric acid, when pure, is a colourless, fuming liquid, but usually is of a faint yellow tinge, through the presence of some of the lower oxides of nitrogen, produced by its partial decomposition. It possesses a faint, though peculiar and characteristic, odour. Nitric acid combines readily with water, with the evolution of heat. On distilling pure nitric acid it commences to boil at 84·5° C., but the boiling-point continues to rise slowly until a temperature of 121° C. is reached; at this stage the acid distils without any further change of temperature, and consists of 68 per cent. of acid together with 32 per cent. of water resulting from the decomposition of the acid, which during the rise in temperature evolves fumes of lower nitrogen oxides. The temperature and composition of this acid of unchanged boiling-point varies, however, with the atmospheric pressure. Thus with a pressure of 70 millimètres only, the boiling-point is between 65° and 70°, and the acid has a composition of 66·7 per cent. The specific gravity of the pure acid at 15° is 1·53, but diminishes with the addition of water; the following table gives the strength of pure nitric acid of various densities :—

Density at 15° C.	Nitric acid in 100 parts by weight	Density at 15° C.	Nitric acid in 100 parts by weight
1·000	0·00	1·381	61·21
1·010	2·00	1·400	65·07
1·022	4·00	1·419	69·20
1·067	11·41	1·442	75·00
1·089	15·00	1·460	80·00
1·120	20·00	1·474	84·00
1·157	25·71	1·488	88·00
1·185	30·00	1·499	91·00
1·237	37·95	1·509	94·00
1·274	43·53	1·520	97·00
1·298	47·18	1·529	99·52
1·331	52·33	1·530	100·00
1·353	56·10	—	—

Nitric acid is readily decomposed by heat; thus the act of boiling dissociates a portion of the acid into water, free oxygen, and nitrogen peroxide. When enclosed in sealed tubes and heated to 250° C. the whole of the acid thus suffers decomposition. The same reaction is caused by passing the acid through a red-hot porcelain tube; for this purpose a long clay tobacco-pipe may be employed, so arranged that the bowl is higher than the stem, which latter is inclined downwards with its mouthpiece under the surface of water in a pneumatic trough. The stem is heated red-hot by a small tube furnace, and the acid poured drop by drop into the bowl of the pipe. Oxygen, nitrogen peroxide, and steam escape at the lower end. Of these the former may be collected in a test-tube, the latter two being respectively dissolved and condensed by the water. Owing to the facility with which nitric acid parts with its oxygen it is an exceedingly powerful oxidising agent. It causes red-hot charcoal to burst into flame on being poured on it. Sulphur, iodine, and phosphorus are readily oxidised by treatment with this acid, and many compounds belonging to what is called the '*-ous*' class (i.e., in a lower state of oxidation), are converted into '*-ic*' compounds. Thus in the presence of hydrochloric acid the addition of a small quantity of nitric acid oxidises ferrous to ferric chloride.

$$\underset{\text{Ferrous chloride}}{2FeCl_2} + \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Ferric chloride.}}{Fe_2Cl_6} + \underset{\text{Nitrogen peroxide.}}{2NO_2} + \underset{\text{Water.}}{2H_2O}.$$

Nitric acid is an extremely corrosive body and rapidly destroys all animal tissues, and hence is used as a powerful caustic; in the diluted state it stains the skin, horn, &c. a bright yellow colour.

194. Action of Nitric Acid on Metals.—The normal action of an acid on a base, by which a salt is formed, has been already described. Nitric acid behaves like other acids, forming salts with bases, which salts are called nitrates. In common with most other acids it decomposes carbonates, yielding nitrates, and liberating carbon dioxide. In the cases of both hydrochloric and sulphuric acids, it has been shown how an easily oxidisable metal, such as zinc, displaces the hydrogen and forms a chloride or a sulphate. Owing to the instability of nitric acid the action in this case is different. The liberation of nascent hydrogen, a powerful reducing agent, in the presence of nitric acid, an easily reduced body, results in the decomposition of the acid with the liberation of nitrogen either in a lower state of oxidation or uncombined. In certain cases the action proceeds even further, and the nitrogen is 'hydrogenised' to ammonia. The precise nature of the change depends on the character of the metal used, and is further governed by the degree of concentration of the acid, and the temperature at which the reaction occurs. Usually a mixture of gases is evolved, in which one or two nitrogen oxides may predominate; but hydrogen is not produced by the action of any metal on nitric acid. The following are examples of the reactions produced by nitric acid and various metals:—

Silver, dissolved slowly in the cold with excess of dilute nitric acid, gives—

$$\underset{\text{Silver.}}{2Ag} + \underset{\text{Nitric acid.}}{3HNO_3} = \underset{\text{Silver nitrate.}}{2AgNO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Nitric acid.}}{HNO_3}.$$

NO is also produced in small quantity. Copper or mercury with moderately concentrated acid (sp. gr. 1·25 to 1·3)—

$$\underset{\text{Copper.}}{3Cu} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Nitric oxide.}}{2NO}.$$

Small quantities of nitrous oxide and nitrogen are also evolved.

With copper and a more dilute acid, the quantities of nitrous acid and nitrogen increase, the former being produced according to the equation—

$$\underset{\text{Copper.}}{4Cu} + \underset{\text{Nitric acid.}}{10HNO_3} = \underset{\text{Copper nitrate.}}{4Cu(NO_3)_2} + \underset{\text{Water.}}{5H_2O} + \underset{\text{Nitrous oxide.}}{N_2O}.$$

With a more highly concentrated acid (sp. gr. 1·42), nitrogen peroxide is formed in large quantity—

$$\underset{\text{Copper.}}{Cu} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Copper nitrate.}}{Cu(NO_3)_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen peroxide.}}{2NO_2}.$$

Using a concentrated acid at a high temperature, considerable quantities of nitrogen are evolved—

$$\underset{\text{Copper.}}{5Cu} + \underset{\text{Nitric acid.}}{12HNO_3} = \underset{\text{Copper nitrate.}}{5Cu(NO_3)_2} + \underset{\text{Water.}}{6H_2O} + \underset{\text{Nitrogen.}}{N_2}.$$

With a dilute acid and zinc nitrous oxide is evolved—

$$\underset{\text{Zinc.}}{4Zn} + \underset{\text{Nitric acid.}}{10HNO_3} = \underset{\text{Zinc nitrate.}}{4Zn(NO_3)_2} + \underset{\text{Water.}}{5H_2O} + \underset{\text{Nitrous oxide.}}{N_2O}.$$

With zinc and a stronger acid—

$$\underset{\text{Zinc.}}{4Zn} + \underset{\text{Nitric acid.}}{9HNO_3} = \underset{\text{Zinc nitrate.}}{4Zn(NO_3)_2} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Ammonia.}}{NH_3}$$

The ammonia combines with the excess of acid employed.

Nitric acid oxidises tin and antimony to hydrated oxides, without the formation of nitrates. Thus the reaction with tin may be represented by—

$$\underset{\text{Tin.}}{5Sn} + \underset{\text{Nitric acid.}}{8HNO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Metastannic acid.}}{H_2Sn_5O_{11},4H_2O} + \underset{\text{Nitric oxide.}}{6NO} + \underset{\text{Nitrogen peroxide.}}{2NO_2}.$$

A portion of the nitric acid may be reduced to lower oxides, or even converted into ammonia.

195. Nitrates.—Most of the metals are vigorously attacked by nitric acid, but gold and platinum are unaffected by it. Nitric acid being monobasic, can form no acid salts, but several basic nitrates exist. The nitrates are soluble in water; many of their number are anhydrous, while others contain water of crystallisation.

The nitrates, like the acid from which they are derived, are powerful oxidising agents; potassium nitrate is used as a source of oxygen in gunpowder, which is a mixture of that compound with sulphur and charcoal.

If charcoal be dropped into melting potassium nitrate, it burns with great brilliancy.

Nitric acid and all the nitrates are decomposed by heat, oxides of the metals remain, and oxygen and nitrogen oxides are driven off. On heating potassium or sodium nitrate, pure oxygen is at first evolved, with the formation of the nitrite thus:—

$$\underset{\text{Potassium nitrate.}}{2KNO_3} = \underset{\text{Potassium nitrite.}}{2KNO_2} + \underset{\text{Oxygen.}}{O_2}$$

On further heating, the nitrate is decomposed, with evolution of a mixture of nitrogen and oxygen, the oxide of the metal remaining.

196. Industrial Applications.—Nitric acid is largely used in the manufacture of sulphuric acid. It is also employed in the dissolving of metals, and in the 'parting' of gold and silver, and in the formation of nitrates of commercial value. It is used in the manufacture of oxalic acid and gun-cotton, also in the preparation of many nitrogenous organic substances. Among these latter are many of the aniline and other sources of dyeing colours.

197. Action of Acids on Gold.—Gold is attacked by neither nitric acid nor hydrochloric acid singly; but a mixture of the two, on being gently heated, dissolves both gold and platinum. (The latter is also unaffected by the single acids.) This mixture of acids is generally termed *aqua regia* (royal water), from its power of thus dissolving 'the king of metals;' its activity depends on the production of nascent chlorine, which combines with gold, forming auric chloride; the reaction may be represented by the following equation, but varies with the different proportions of hydrochloric and nitric acids which may be used:—

$$\underset{\text{Nitric acid.}}{3HNO_3} + \underset{\text{Hydrochloric acid.}}{9HCl} + \underset{\text{Gold.}}{2Au} = \underset{\text{Nitrogen oxychloride.}}{3NOCl} + \underset{\text{Water.}}{6H_2O} + \underset{\text{Gold chloride.}}{2AuCl_3}.$$

198. **Nitric Anhydride** is an unstable body, and is rarely prepared: it readily unites with water and forms nitric acid :—

$$\underset{\text{Nitric anhydride.}}{N_2O_5} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitric acid.}}{2HNO_3}.$$

Nitrogen Monoxide.—Formula, N_2O. Molecular weight, 43·98. Density, 21·99. Specific gravity, 1·527.

199. **Preparation.**—As previously stated (paragraph 194), nitrogen monoxide, or nitrous oxide, may be prepared on gently heating together zinc and dilute nitric acid. A much more convenient method of obtaining nitrogen monoxide is by the action of heat on ammonium nitrate, which is decomposed in a manner similar to that in which ammonium nitrite, NH_4NO_2, is separated into water and nitrogen; the nitrate, however, contains another atom of oxygen (its formula being NH_4NO_3), which is evolved in combination with the nitrogen :—

$$\underset{\text{Ammonium nitrate.}}{NH_4NO_3} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen monoxide}}{N_2O}.$$

This equation should be compared with that representing the decomposition of ammonium nitrite.

The ammonium nitrate, on being gently heated in a glass flask, quickly melts, after which the evolution of the gas soon commences. Too violent a heat must not be applied, as if the temperature be raised too high, the gas is produced with almost explosive rapidity, and nitric oxide is formed in considerable quantity. The gas is collected in a pneumatic trough over warm water.

200. **Manufacture.**—Nitrous oxide is made on the large scale in the same manner as the small, by the decomposition of ammonium nitrate. It is freed from traces of chlorine by being passed through a solution of caustic soda, and from nitric oxide by treatment with ferrous sulphate solution. The purified gas is then condensed under pressure to the liquid form, and stored in wrought-iron cylinders.

201. **Properties.**—Nitrogen monoxide is colourless, has a faint, sweetish smell and taste; it is soluble in cold water;

1 volume at 15° C. dissolves 0·77 volume of the gas. It may be condensed to a liquid by a pressure of thirty atmospheres at 0° C., or at ordinary pressures at a temperature of $-99°$ C. Nitrogen monoxide supports combustion almost as vigorously as oxygen; oxides are formed, and nitrogen liberated. Carbon thus forms carbon dioxide :—

$$\underset{\text{Carbon.}}{C} + \underset{\text{Nitrogen monoxide.}}{2N_2O} = \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Nitrogen.}}{2N_2}.$$

At a red heat nitrogen monoxide is decomposed into nitrogen and oxygen; this decomposition into free oxygen and nitrogen is necessary before bodies can burn in the gas: if the heat of the combustion is not sufficient to effect this change, burning does not go on. Thus feebly burning sulphur is extinguished by nitrous oxide, but when burning brightly it continues to do so almost as vividly as in oxygen.

The two gases, oxygen and nitrogen monoxide, may, however, be readily distinguished from each other by the much greater solubility of the latter gas, and also by the difference in their behaviour with nitric oxide, to which reference will again be made. In actual analysis the presence of a residue of nitrogen after combustion would also distinguish nitrous oxide from oxygen.

202. Industrial Applications.—Nitrogen monoxide behaves as an anæsthetic when breathed (*i.e.* a substance which causes insensibility to pain), and is largely used for this purpose in minor surgical and especially dental operations. Some four or five gallons of the gas are sufficient in most cases to produce total insensibility; before this stage, particularly if mixed with air or oxygen, it in many persons causes a kind of intoxication, often accompanied by violent fits of laughter; because of this it has received the popular name of 'laughing gas.'

203. Composition.—On gently heating potassium in nitrous oxide, the metal commences to burn, with the formation of solid potassium peroxide :—

$$\underset{\text{Nitrous oxide.}}{4N_2O} + \underset{\text{Potassium.}}{2K} = \underset{\text{Potassium peroxide.}}{K_2O_4} + \underset{\text{Nitrogen.}}{4N_2}.$$

For the purpose of this experiment a U-tube of difficultly fusible glass is prepared, with one limb three inches and the other about fifteen in length. A bulb is first blown on what is to be the shorter limb. Into this a pellet of potassium about the size of a pea is introduced. The tube is arranged to stand inverted, with its open end under the surface of some mercury in a pneumatic trough, and is filled by displacement with pure nitrous oxide. (This may be effected by pushing a piece of india-rubber tubing into the U-tube, so that its end reaches right round the bend into the bulb.) By tilting the tube with its open end under the mercury, some of the gas is allowed to escape so that the mercury in the inverted U-tube stands considerably above the level of that in the trough, on the tube being replaced in the vertical position. This height is then carefully noted. The potassium is next gently heated with a bunsen; it melts and burns until the whole of the oxygen of the nitrous oxide is consumed. At the same time the mercury descends in the other limb, as a result of the expansion of the gas through heat; but if the length of tube be properly arranged, none of the gas will escape. Combustion being over, and the gas having regained its previous temperature, it is found to have the same volume as that before the reaction had occurred. We thus see that nitrous oxide yields, on decomposition, its own volume of nitrogen, or that a molecule of the oxide yields a molecule of nitrogen gas.

Another method of determining the composition of nitrogen monoxide is by explosion in a eudiometer with hydrogen in excess. Thus if ten volumes of nitrous oxide be placed in the eudiometer and twelve volumes of hydrogen added, and then the mixture exploded by passing an electric spark, the following reaction occurs :—

$$\underset{\text{Nitrous oxide.}}{N_2O} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Nitrogen.}}{N_2} + \underset{\text{Water.}}{H_2O.}$$

There will consequently be a reduction of volume by ten measures. In the next place it is necessary to determine the excess of hydrogen remaining : this is effected by adding excess of oxygen, say four volumes, and again exploding; there will be a diminution of three volumes, consisting, we know, of two

volumes of hydrogen and one volume of oxygen; thirteen volumes of gas will still remain in the eudiometer. Of this we know three are oxygen, because they were added in measured quantity; the remaining ten consist of nitrogen. In the first explosion $12 - 2 = 10$ volumes of hydrogen combined with the oxygen of the nitrous oxide; we know, therefore, that the quantity of oxygen it contained, if measured in the free state, would amount to five volumes. The experiment proves then that ten volumes of nitrous oxide yield ten volumes of nitrogen, and oxygen equivalent to five volumes to hydrogen to form water; or, two molecules of nitrous oxide yield two molecules of nitrogen and one molecule of oxygen, according to the equation:—

$$2N_2O = 2N_2 + O_2.$$

This may be further proved by repeatedly passing nitrous oxide through a red-hot tube, when two volumes increase to three.

Nitric Oxide or Nitrogen Dioxide.—Formula, NO (or N_2O_2). Molecular weight, 29·97. Density, 14·98. Specific gravity, 1·039.

204. **Preparation.**—As already described, nitric oxide, in a more or less pure condition, is produced by the action of copper on moderately concentrated nitric acid. The preparation is effected in an ordinary gas flask fitted with thistle-funnel and delivery-tube; it is collected over water. The proportion of impurities increases as copper nitrate is formed; it is well, therefore, to employ acid and metal in considerable excess, using only the earlier quantities of gas collected. To prepare pure nitric oxide, the gas is passed into a cold concentrated solution of ferrous sulphate, by which it is absorbed. This solution on being heated yields the gas in its pure state.

205. **Properties.**—This gas is colourless, but immediately on coming in contact with air combines with the oxygen and forms higher nitrogen oxides of a ruddy tint; from its possessing these properties it is difficult to either taste or smell it. The strong odour observed during its preparation is that of these higher oxides.

Nitric oxide has until recently been considered a permanent gas, but was liquefied by Cailletet at $-11°$ C. by a pressure of 104 atmospheres. It is much more stable than nitrogen monoxide, and may be subjected to even a red heat without decomposition; consequently a lighted taper does not burn in it.

Phosphorus, when feebly ignited, is also extinguished, but if strongly ignited burns with almost as much brilliancy as in pure oxygen:—

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Nitric oxide.}}{10NO} = \underset{\text{Phosphorus pentoxide.}}{2P_2O_5} + \underset{\text{Nitrogen.}}{5N_2}.$$

A mixture of carbon disulphide vapour and nitric oxide burns with an intense bluish light.

Nitric oxide is not itself combustible. One of its most striking properties is the power it possesses of spontaneously combining with oxygen on the two being brought together; the resultant ruddy gas is a mixture of nitrogen trioxide and peroxide in varying proportions:—

$$4NO + O_2 = 2N_2O_3, \text{ Nitrogen trioxide.}$$
$$2NO + O_2 = 2NO_2, \text{ Nitrogen peroxide.}$$

As nitrous oxide does not possess this property, this reaction serves to distinguish the one gas from the other. This may be demonstrated by taking a jar of pure oxygen and pouring up into it in the pneumatic trough pure nitric oxide from another jar, bubble by bubble. With each addition of nitric oxide red fumes are formed, which gradually disappear, and the water rises in the jar. If the two gases be pure, the addition of nitric oxide in this manner causes the oxygen to disappear entirely. If nitric oxide is added in a similar manner to nitrous oxide, no red fumes nor diminution of volume is produced: the gases are without action on each other.

The reason of the above reaction is that, while nitric oxide is but feebly soluble in water (water dissolves about one-twentieth of its volume), the higher oxides produced are very soluble, and are thus absorbed as rapidly as formed.

206. Industrial Applications.—Owing to its property of directly combining with atmospheric oxygen to form the

higher oxides, nitric oxide fulfils most important functions in the manufacture of sulphuric acid. These, together with its preparation for that purpose, are explained fully in the description of sulphuric acid manufacture.

207. Composition.—The composition of nitric oxide may be determined by heating potassium in the gas in a manner similar to that employed with nitrous oxide. In this case the remaining volume of nitrogen is one-half that of the original gas. By strongly heating charcoal in nitric oxide, the gas is decomposed with the formation of carbon dioxide and liberation of free nitrogen. This change having been effected in a suitable vessel, the volume of gas is found to be unaltered. On heating the residual mixture with potassium hydrate, half the total volume is thus absorbed, leaving the other moiety of free nitrogen. Carbon dioxide contains its own volume of oxygen, therefore two volumes of nitric oxide are shown to yield on decomposition one volume each of nitrogen and oxygen, a change which agrees with the equation :—

$$\underset{\text{Nitric oxide.}}{2NO} = \underset{\text{Nitrogen.}}{N_2} + \underset{\text{Oxygen.}}{O_2}.$$

The density of the gas necessitates its being represented by the formula NO, but as so written the nitrogen has an unsatisfied valency bond, thus $-N{=}O$. This has led some chemists to assume that the normal molecule of nitric oxide is really N_2O_2, in which case the valency difficulty is obviated; thus $O{=}N{-}N{=}O$; and hence the name nitrogen dioxide has been adopted and is still at times used. Against this view there is the fact that, even down to a temperature of $-70°$ C., the gas has a density corresponding to the formula NO Further, it is a general rule that the more atoms a molecule contains, the more unstable it is. Nitric oxide is more stable than nitrogen monoxide, and this, therefore, is an additional reason for considering NO to be its true formula. As we have already seen, it is not an absolute necessity for the existence of any compound that all the valency links of each element it contains shall be satisfied.

Nitrogen Trioxide.—Formula, N_2O_3. Molecular weight, 75·90. Density, 37·95.

Nitrous Acid.—Formula, HNO_2.

208. Preparation.—This gas is one of the products of the oxidation of nitric oxide. By passing a mixture of dry nitric oxide and nitrogen peroxide (evolved by heating arsenic trioxide, As_2O_3, with nitric acid, density 1·3) through a red-hot tube, nearly pure nitrogen trioxide is formed. This may be condensed by a freezing mixture to a volatile blue liquid, from which red fumes are rapidly evolved.

209. Properties.—Nitrogen trioxide dissolves in a small quantity of water to form nitrous acid. This is, however, so unstable that even the addition of more water causes its decomposition :—

$$\underset{\text{Nitrous anhydride, or nitrogen trioxide.}}{N_2O_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitrous acid.}}{2HNO_2.}$$

If the gas be passed into a solution of caustic potash or ammonia, it is absorbed, and a nitrite is formed :—

$$\underset{\text{Nitrous anhydride.}}{N_2O_3} + \underset{\text{Potassium hydrate.}}{2KHO} = \underset{\text{Potassium nitrite.}}{2KNO_2} + \underset{\text{Water.}}{H_2O.}$$

Nitrites of the alkaline metals are also formed when the nitrates are heated until one atom of oxygen is expelled from the molecule.

Nitrites are decomposed by stronger acids, with evolution of nitrogen trioxide :—

$$\underset{\text{Potassium nitrite.}}{2KNO_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Nitrogen trioxide.}}{N_2O_3.}$$

This represents the simplest action of acids, but in the presence of water, two molecules of nitrogen trioxide undergo further decomposition, re-arranging their oxygen so as to form nitric oxide and nitric acid.

Nitrogen Peroxide.—Formula, NO_2. Molecular weight, 45·93. Density, 22·96.

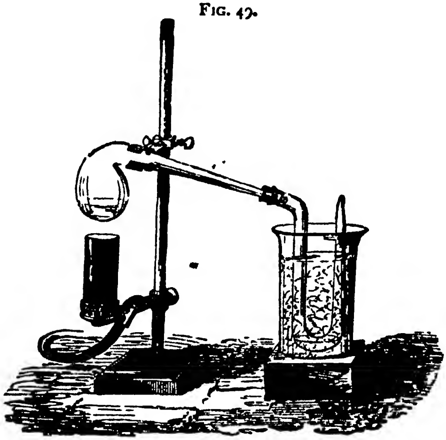
210. Preparation.—This body is the principal substance formed when nitric oxide is oxidised by the action of excess of

oxygen. It is conveniently prepared by the action of heat on carefully dried lead nitrate :—

$$\underset{\text{Lead nitrate.}}{2Pb(NO_3)_2} = \underset{\text{Lead oxide.}}{2PbO} + \underset{\text{Nitrogen peroxide.}}{4NO_2} + \underset{\text{Oxygen.}}{O_2}.$$

The salt is heated in a small glass retort, fig. 49, the stem of which is connected to a U-tube immersed in a freezing

FIG. 49.



mixture of ice and salt. At first a greenish liquid distils over, due to the presence of minute traces of moisture. These being expelled, the anhydrous peroxide condenses as colourless prismatic crystals, and may be collected as such by changing at this stage the U-tube for another which is perfectly dry.

211. Properties.—Obtained in the manner just described, nitrogen peroxide consists of crystals which melt at −10° C., into an almost colourless liquid; with a rise of temperature, this liquid deepens in colour through various shades of orange, until at ordinary temperatures it is a deep red. The liquid boils at 22° C., emitting a vapour of a reddish-brown colour, which has the characteristic odour of nitrous fumes. The colour of this gas darkens with an increase of temperature until, at about 38°, it is almost opaque. This change in colour is probably accompanied by a dissociation

of the molecule : it is probable that at temperatures just above the boiling-point a portion at least of the gas exists as molecules, represented by N_2O_4 ; these become decomposed with the higher temperature into NO_2 molecules. The dissociation is absolutely complete above 154° C.

Nitrogen peroxide supports the combustion of a taper ; it is very soluble in water, forming nitric acid and nitric oxide, which latter, in the presence of free oxygen, is converted into the peroxide, which is again acted on by the water, and thus by a series of changes the whole of the nitrogen peroxide is converted into nitric acid.

212. Other Nitrogen Compounds.—Passing mention must be made of other compounds of nitrogen. Among these are :—

Hydroxylamine, NH_2HO.—This body, known also as oxy-ammonia, may be viewed as ammonia in which one of the atoms of hydrogen is replaced by the hydroxyl semi-molecule, HO. It may be prepared by the action of nascent hydrogen on some of the oxides of nitrogen. Thus it has been explained that zinc and nitric acid yield ammonia ; employing tin, hydrochloric acid, and a nitrate, the nascent hydrogen from the action of the acid on the tin, attacks the nitrate and reduces it, with the formation of hydroxylamine, which combines with the hydrochloric acid and forms hydroxylamine hydrochloride, NH_2HOHCl. This salt is procured in the pure state by processes of crystallisation, and from it hydroxylamine in a state of solution may be obtained. Hydroxylamine is a volatile and very unstable base, and is of interest as one of the very numerous class of bodies termed substitutive ammonias, which are produced by the replacement of the hydrogen of ammonia by various radicals, the majority of which are organic. It should be observed that hydroxylamine combines with the whole of the hydrochloric acid molecule, and not simply the chlorine ; in this respect it is similar to ammonia :—

$$\underset{\text{Hydroxylamine.}}{NH_2HO} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Hydroxylamine hydrochloride.}}{NH_2HOHCl, \text{ or } NH_3HOCl.}$$

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ammonium chloride.}}{NH_3HCl \text{ or } NH_4Cl.}$$

The radical which must be viewed as the analogue of the metals potassium or sodium in this case, is the hypothetic NH_2HOH, or NH_3HO (which might be called 'hydroxyl-ammonium') which corresponds to the also hypothetic NH_3H or NH_4, ammonium.

Chloride of Nitrogen, $NHCl_2$ or NCl_3.—On inverting a jar of chlorine over a dilute solution of ammonium chloride contained in a leaden dish, drops of an oily yellow liquid are gradually formed and collect at the bottom of the dish. These drops consist of chloride of nitrogen, which is probably the most violent and dangerously explosive compound known. Contact with the slightest trace of grease or turpentine and other substances causes its explosion with terrible violence. The preparation of chloride of nitrogen has been frequently attended with fatal results; its production should therefore not on any account be attempted except by the most skilled experimentalists.

The analysis of chloride of nitrogen is most difficult because of its explosive nature. It is probably a substitution compound formed by the replacement by chlorine of either the whole or a portion of the hydrogen of ammonia. There may be more than one of these chlorides of nitrogen.

Cyanogen, C_2N_2.—This body is a gas having the density 25·98, and therefore consisting of two atoms each of carbon and nitrogen in the molecule. It is readily prepared by heating mercury cyanide, $Hg(CN)_2$:—

$$\underset{\text{Mercury cyanide.}}{Hg(CN)_2} = \underset{\text{Mercury.}}{Hg} + \underset{\text{Cyanogen.}}{C_2N_2}.$$

The gas is soluble in water, possesses a peculiar odour, and is readily inflammable, burning with a characteristic purplish-coloured flame. The principal interest in cyanogen is that its semi-molecule, CN, is a most important radical; it forms a series of compounds very similar in chemical construction to those of halogens. Thus we have hydrocyanic acid, HCN, and cyanides, KCN, &c., in which the group CN is found to act as a mineral radical, and thus fill a place analogous to that occupied by chlorine. This radical is of such importance that, like ammonium, it has received a special symbol, Cy

instead of CN. The constitution of this radical is shown graphically thus —C≡N. Below are given the corresponding formulæ of hydrochloric and hydrocyanic acids :—

$$H—Cl \qquad H—C \equiv N.$$

Carbon and nitrogen cannot be made to combine directly when heated alone. But in the presence of potassium at a high temperature combination ensues, and potassium cyanide, KCN or KCy, is formed ; from this body hydrocyanic acid is obtained.

Hydrocyanic Acid, HCN or HCy.—Hydrocyanic acid is a volatile liquid, having an odour somewhat resembling that of bitter almonds. It is miscible with water in all proportions, and may be obtained by heating either potassium cyanide or potassium ferrocyanide, K_4FeCy_6, with dilute sulphuric acid, and distilling. The latter is the more convenient salt to use, and when the aqueous acid is required the vapours produced by distillation are carried over and absorbed in water. Hydrocyanic acid is one of the most poisonous substances known, the inhalation of small quantities of its vapour being sufficient to cause death. It reddens litmus, but is so feebly acid that it is displaced from its combination with bases by even so weak an acid as carbonic acid ; hence potassium cyanide has always a feeble odour of hydrocyanic acid, caused by its decomposition by the carbon dioxide present in atmospheric air. Hydrocyanic acid is monobasic, and forms an extensive series of salts, which, with the exception of those of the alkalies and alkaline earths, are insoluble in water. Many of the metals produce with the alkaline cyanides soluble double cyanides, as $AgKCy_2$ and others. These are readily decomposed by a dilute acid, but a second class of double cyanides is known in which a much more intimate union of the two cyanides occurs. Among these is potassium ferrocyanide, K_4FeCy_6 or $(KCy)_4FeCy_2$. This body is not decomposed by the addition of a dilute acid, but yields a body having the composition H_4FeCy_6, which possesses well-defined acid properties, and has been named ferrocyanic acid. A number of acids of this type exist.

The alkaline cyanides readily combine with oxygen, forming cyanates, as potassium cyanate, KCNO; they are in consequence powerful reducing agents.

CHAPTER XVI

SULPHUR AND SULPHURETTED HYDROGEN

Sulphur.—Symbol, S. Atomic weight, 31·98. Specific gravity of native crystals, 2·07. Molecular weight at 482° C., 191·88. Observed density, 95·85. Molecular weight at 1040° C., 63·96. Observed density, 32·18. Melting-point, 113°. Boiling-point, 446°.

213. **Occurrence.**—Sulphur is a widely distributed element, occurring in the free state in Sicily, Iceland, and other volcanic districts. Many of the ores from which metals are derived are compounds of these metals with sulphur; in the list of these are included the sulphides of lead, copper, mercury, and zinc. These native metallic sulphides are frequently characterised by their possessing a bright metallic lustre. One of the most commonly occurring of such sulphides is that of iron, termed iron pyrites, and having the formula FeS_2. This substance is not worked for iron; but as sulphur is largely extracted from it as a commercial operation, it is frequently termed 'sulphur ore.'

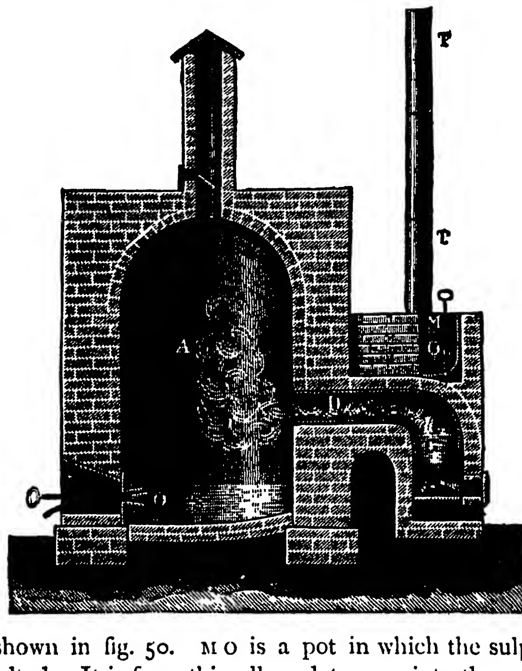
The sulphates are another important class of natural bodies containing sulphur. Of these gypsum or calcium sulphate, $CaSO_4$, and barium sulphate, $BaSO_4$, occur in large quantity.

Many organic bodies contain sulphur as an essential ingredient, especially albumin. Hence, in their putrefaction, sulphur compounds are among the products, and are always present in sewage gases, &c. White of egg is an almost pure form of albumin, and owes its odour when rotten to the presence of a compound of sulphur and hydrogen.

214. **Extraction.**—The free sulphur collected in volcanic districts is contaminated with earthy impurities. These are

removed on the spot by melting the sulphur from them; or, in the poorer samples, by the process of distillation. For this purpose the rocky matter containing the sulphur is arranged in heaps, and then set fire to at the bottom. A portion of the sulphur in burning melts out the remainder. The crude sulphur thus obtained is further purified on its arrival in this country by being a second time distilled in an apparatus such

FIG. 50.



as is shown in fig. 50. M O is a pot in which the sulphur is first melted. It is from this allowed to run into the cast-iron retort G; in this it is distilled by the action of heat, and its vapour finds its way through D into the brickwork chamber A. The heat being slowly applied, the first portions of vapour entering the chamber condense to the solid form, and fall to the bottom as a fine dust, which constitutes what is commercially known as 'flowers of sulphur.' At a higher temperature

the walls of the chamber become heated; the sulphur condenses on them in the liquid form, and collects as a liquid mass, S, on the floor of the chamber. On opening the plug at O, the sulphur is drawn off into cylindrical wooden moulds and allowed to solidify. In this manner is produced the roll 'brimstone' of commerce.

To obtain sulphur from sulphur ore—iron pyrites—a layer of brushwood is first deposited, on which the ore is built into mounds, and covered over with a coating of previously burnt ore. Openings are made at the top and near the bottom; the brushwood is lighted, and with the heat the sulphur is expelled from the ore, according to the equation:—

$$\underset{\text{Ferric sulphide.}}{3FeS_2} = \underset{\text{Triferric tetrasulphide.}}{Fe_3S_4} + \underset{\text{Sulphur.}}{S_2}.$$

In this mode of extraction a considerable waste of sulphur occurs, through its being oxidised into sulphur dioxide.

215. Properties.—Sulphur is a lemon-yellow solid. It is insoluble in water, and therefore possesses no taste, but has a faint odour. The rolls of sulphur are extremely brittle, and as it is also a bad conductor of heat, the warmth of the hand is often sufficient to cause a roll to fall in pieces when held. It melts at a temperature of 113° C. to a limpid yellow liquid, which, if allowed to cool slowly, deposits long prismatic needle-like crystals. To obtain these the sulphur should be melted in a crucible, at as low a temperature as possible. The crucible is then set aside until a solidified crust has formed on the surface; this is pierced in two places with a hot iron, and as much as possible of the still melting sulphur run out. On then removing the crust a fine crop of crystals is seen within. These are at first perfectly transparent, but after a time become opaque, through each breaking up into a number of minute rhombic octahedral crystals. The external form is still retained, but little coherence remains.

If sulphur be dissolved in carbon disulphide, and the liquid then allowed to evaporate, the sulphur is obtained in octahedral crystals of the rhombic system. These are permanent

in air, and the form is that in which native sulphur crystals occur.

There are, then, two distinct forms in which sulphur crystallises; the one from fusion, the other from solution. The latter are permanent, the former unstable, gradually changing into the latter. The two crystalline forms are also distinguished from each other by their specific gravity; that of the prismatic crystals is 1·96, and that of the octahedral or permanent form is 2·07.

In addition to these two varieties, there is another known as plastic sulphur, whose properties widely differ from those of either. If, instead of allowing the limpid yellow liquid, produced as a result of melting sulphur, to cool, the application of heat be continued, a remarkable series of changes ensues. The colour gradually darkens as the temperature rises; at the same time the liquid becomes thicker, until, at a temperature of 180° C., the mass is almost black, and so viscid that the vessel may be momentarily held inverted without the sulphur running out. With a further increase of temperature, the sulphur again becomes liquid, but remains of a much thicker consistency than it possessed on first melting. If while in this state it be poured into water, a soft, indiarubber-like mass is produced, of a yellowish-brown tint, which may be drawn out into long threads. The difference between these and the common brittle form of sulphur is very striking. In a few hours it loses its tenacity, becoming again opaque and brittle. Plastic sulphur is insoluble in carbon disulphide, but on once more acquiring the brittle state it becomes partly soluble, leaving, however, a brown powder, which remains insoluble until converted by fusion into the ordinary crystalline variety.

In addition to the forms of sulphur described, there are some other varieties, which, however, are not of great importance.

At the temperature of 446° C. sulphur boils, with the formation of a dark brownish-red vapour, having, at temperatures up to about 480°, a density of 95·85, from which a molecular weight of 191·88 is declared. This weight agrees with that required for a hexatomic molecule, and, accordingly, it is con-

cluded that at this temperature the molecules of sulphur each contain six atoms. With an increase in temperature, the density gradually diminishes until, at 1040°, the density is 32·18, a figure which closely agrees with that theoretically required for a diatomic molecule. At the intermediate temperatures sulphur probably exists as an intermixture of diatomic and hexatomic molecules.

Sulphur is an element which enters vigorously into combination with other elements; it is on the one hand inflammable, and on the other supports the combustion of various bodies. Thus on being heated in either air or oxygen, sulphur burns with either a pale-blue or more vivid lilac-coloured flame, at the same time emitting a suffocating odour, the reaction being represented by :—

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Oxygen.}}{2O_2} = \underset{\text{Sulphur dioxide.}}{2SO_2}.$$

Traces of a higher oxide of sulphur are also formed, the formation of which will be subsequently described.

If, in the next place, sulphur be raised in a flask to the boiling-point so as to produce an atmosphere of sulphur vapour, a fine coil of copper enters into vivid combustion on being introduced into this sulphur atmosphere. Many other metals combine readily with sulphur, especially noticeable among them being silver, which forms a coating of sulphide at ordinary temperatures. This is the more remarkable, as silver is a metal which does not readily enter into combinations.

216. Industrial Applications.—The principal use of sulphur is indirectly in the manufacture of sulphuric acid. It is employed, although to a much less extent than formerly, in the production of matches. Sulphur also forms one of the most important ingredients of gunpowder.

217. Sulphides.—With the exception of those of the alkalies and alkaline earths, the sulphides are insoluble in water. The metallic sulphides have almost invariably corresponding formulæ to the oxides, sulphur acting in these bodies as a dyad element. Two compounds of sulphur with hydrogen are known, having respectively the formulæ SH_2 and S_2H_2.

They are analogous in composition to the corresponding oxides, OH_2 and O_2H_2. The latter sulphide, hydrogen persulphide, S_2H_2 is, like the peroxide, an unstable body, and has little practical importance. The normal sulphide, SH_2, requires a more extended description.

Sulphuretted Hydrogen.—Formula, SH_2. Molecular weight, 33·98. Density, 16·99. Specific gravity, 1·1912.

218. **Occurrence.**—This compound, which is also sometimes known by the name of hydrosulphuric acid, is found free in volcanic districts, and also in the waters of certain mineral springs, as those at Harrogate.

219. **Preparation.**—It is formed when hydrogen is passed into sulphur vapour, but only in small quantities.

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Sulphuretted hydrogen.}}{2SH_2}.$$

Sulphuretted hydrogen is commonly prepared for use in the laboratory by the action of dilute sulphuric acid on a sulphide, that of iron being usually chosen. The reaction goes on readily, without the application of heat, the iron displacing the hydrogen, and the sulphur and hydrogen uniting.

$$\underset{\substack{\text{Ferrous}\\\text{sulphide.}}}{FeS} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{FeSO_4} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{SH_2}.$$

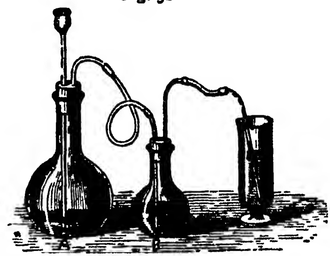
A similar apparatus is employed to that used for the preparation of hydrogen from dilute sulphuric acid and zinc. Ferrous sulphide usually contains metallic iron as an impurity, and consequently the evolved sulphuretted hydrogen contains free hydrogen. For the great majority of purposes this is no detriment, but when pure sulphuretted hydrogen is required, antimonious sulphide is gently heated with a concentrated solution of hydrochloric acid :—

$$\underset{\substack{\text{Antimonious}\\\text{sulphide.}}}{Sb_2S_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\substack{\text{Antimonious}\\\text{chloride.}}}{2SbCl_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3SH_2}.$$

Sulphuretted hydrogen is soluble in cold water, one volume at 15° C. dissolving 3·23 volumes of the gas. This solution is

of great importance in the laboratory, and is prepared by passing the gas from the generating flask A, fig. 51, through a wash-bottle, B, and then into a beaker or other vessel containing water, until the water is saturated with the gas.

Fig. 51



220. Properties. — Sulphuretted hydrogen is a colourless gas, having a characteristic odour of rotten eggs. The solution in water has a corresponding odour, and sweetish taste. It is inflammable, and a non-supporter of combustion. With excess of oxygen, sulphur dioxide and water are produced by the burning of this gas, according to the equation :—

$$\underset{\text{Sulphuretted hydrogen.}}{2SH_2} + \underset{\text{Oxygen.}}{3O_2} = \underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Water.}}{2H_2O.}$$

On holding above the flame a rod dipped in ammonia the sulphur dioxide forms a solid compound, named ammonium sulphite. The fumes of this body are evidence of the presence of sulphur dioxide—

$$\underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Ammonium hydrate.}}{2NH_4HO} = \underset{\text{Ammonium sulphite.}}{(NH_4)_2SO_3} + \underset{\text{Water.}}{H_2O.}$$

Sulphuretted hydrogen produces no fumes with ammonia. More conclusive evidence of the presence of sulphur dioxide as one of the products of combustion is afforded by holding the nose above the flame, when its characteristic odour is observed. When the supply of air is limited, as when the gas burns in a jar, the sulphur is in great part deposited, the hydrogen only being burned.

$$\underset{\text{Sulphuretted hydrogen.}}{2SH_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Sulphur.}}{S_2} + \underset{\text{Water.}}{2H_2O.}$$

Under a pressure of seventeen atmospheres, sulphuretted hydrogen condenses to a colourless liquid, whose boiling and freezing points are respectively —62° and −86° C.

Water at ordinary temperatures dissolves about 3·25 volumes of the gas, forming a solution which changes the colour of litmus to a port-wine tint; hence the employment of the name hydrosulphuric acid.

221. Composition.—Sulphuretted hydrogen is decomposed into sulphur and hydrogen by being subjected to a red heat. Using a special U-tube, such as that employed for the determination of the composition of nitrous oxide gas by the action on it of potassium, the composition of sulphuretted hydrogen is thus determined. The bulb of the tube is charged with granulated tin, and then the instrument filled with sulphuretted hydrogen over mercury, and heated exactly as in the nitrous oxide experiment. On heating the tin, stannous sulphide (SnS) is formed, and at the conclusion of the reaction a volume of hydrogen is found to remain, exactly equal to that of sulphuretted hydrogen taken. Sulphuretted hydrogen, therefore, yields its own volume of hydrogen, a fact represented in the following molecular equation:—

$$\underset{\text{Sulphuretted hydrogen.}}{SH_2} + \underset{\text{Tin.}}{Sn} = \underset{\text{Stannous sulphide.}}{SnS} + \underset{\text{Hydrogen.}}{H_2}.$$

222. Acidity of Sulphuretted Hydrogen.—The action of sulphuretted hydrogen on litmus shows that the gas possesses acid properties. These are, however, so feeble that in the case of soluble sulphides carbon dioxide is able to displace the sulphuretted hydrogen. The sulphides of all the metals are insoluble in water, with the exception of those of calcium, barium, strontium, magnesium, sodium, and potassium, and a few of the very rare metals. The insolubility of the other metallic sulphides affords to the analyst a very valuable means of separating those metals from the group above mentioned.

Whenever two compounds are brought together which respectively contain elements that by their union are capable of forming an insoluble compound, that compound will usually be produced; so that, although sulphuretted hydrogen is a weak acid, it is thus able to displace stronger ones from many metals. A current of sulphuretted hydrogen passed through

a solution of copper chloride precipitates copper sulphide; thus—

$$\underset{\text{Copper chloride.}}{CuCl_2} + \underset{\text{Sulphuretted hydrogen.}}{H_2S} = \underset{\text{Copper sulphide.}}{CuS} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

And this although hydrochloric acid is so much more powerful in its properties.

These sulphides have, in many cases, characteristic colours, by which they are immediately recognised. They possess the further advantage of being divided into two groups, one of which is soluble in dilute hydrochloric acid, the other not so.

Thus, if sulphuretted hydrogen be passed through acidulated solutions of the following substances—arsenious anhydride, copper sulphate, lead acetate, tartar emetic or antimony chloride, zinc sulphate, and ferrous sulphate—the following results are observed:—

$$\underset{\text{Arsenious anhydride.}}{As_2O_3} + 3SH_2 = 3H_2O + \underset{\text{Arsenious sulphide.}}{As_2S_3}, \text{ Lemon Yellow Precipitate.}$$

$$\underset{\text{Copper sulphate.}}{CuSO_4} + SH_2 = H_2SO_4 + \underset{\text{Copper sulphide.}}{CuS}, \text{ Black Precipitate.}$$

$$\underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + SH_2 = \underset{\text{Acetic acid.}}{2HC_2H_3O_2} + \underset{\text{Lead sulphide.}}{PbS}, \text{ Black Precipitate.}$$

$$\underset{\text{Antimony chloride.}}{2SbCl_3} + 3SH_2 = 6HCl + \underset{\text{Antimony sulphide.}}{Sb_2S_3}, \text{ Orange Precipitate.}$$

$$\left.\begin{array}{l} ZnSO_4 \text{ Zinc Sulphate} \\ FeSO_4 \text{ Iron Sulphate} \end{array}\right\} \text{In acid solution } SH_2 \text{ produces no precipitate.}$$

The passage of sulphuretted hydrogen through fresh portions of zinc and iron sulphates rendered slightly alkaline by the addition of ammonium chloride and ammonia, yields:—

$$\underset{\text{Zinc sulphate.}}{ZnSO_4} + SH_2 = H_2SO_4 + \underset{\text{Zinc sulphide.}}{ZnS}, \text{ White Precipitate.}$$

$$\underset{\text{Iron sulphate.}}{FeSO_4} + SH_2 = H_2SO_4 + \underset{\text{Iron sulphide.}}{FeS}, \text{ Black Precipitate.}$$

On the addition of a few drops of hydrochloric acid to these precipitates they are immediately redissolved.

The sulphides are not only well-defined salts, but also a series of bodies of great importance to the analyst.

Sulphuretted hydrogen may be viewed as a dibasic acid, and in fact forms a series of well-marked bodies which may be regarded as acid or hydric sulphides. Among these we have potassium hydrosulphide, KHS, and ammonium hydrosulphide, AmHS, a liquid produced by saturating a solution of ammonium hydrate with sulphuretted hydrogen.

223. Decompositions of Sulphuretted Hydrogen.—The great affinity of hydrogen and chlorine for each other causes the decomposition of the sulphuretted hydrogen. Thus, if a jar of each of the gases be brought together, hydrochloric acid is at once formed and sulphur deposited according to the equation—

$$\underset{\text{Sulphuretted hydrogen.}}{2SH_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Sulphur.}}{S_2}.$$

Free oxygen has no action on the dry gas, but in the presence of water a slow oxidation takes place. Hence an aqueous solution of sulphuretted hydrogen becomes turbid on exposure to the atmosphere, through the separation of sulphur and the formation of water—

$$\underset{\text{Sulphuretted hydrogen.}}{2SH_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Sulphur.}}{S_2} + \underset{\text{Water.}}{2H_2O}.$$

A curious and interesting reaction takes place between sulphuretted hydrogen and sulphur dioxide when moist; on bringing together the mouths of two jars containing these gases they decompose each other, with the separation of sulphur and formation of water. Apparently the decomposition is in part determined by the affinity of the sulphur atoms for each other, in the same way as the affinity of oxygen atoms causes the mutual decomposition of hydroxyl and silver oxide. In the above reaction an acid of sulphur known as pentathionic acid is also formed—

$$\underset{\text{Sulphur dioxide.}}{10SO_2} + \underset{\text{Sulphuretted hydrogen.}}{10SH_2} = \underset{\text{Sulphur.}}{5S_2} + \underset{\text{Water.}}{8H_2O} + \underset{\text{Pentathionic acid.}}{2H_2S_5O_6}.$$

This reaction is of interest as being that by which probably much of native sulphur has been deposited, both of these gases being emitted from volcanoes.

224. Other Sulphur Compounds.—Among the compounds of sulphur with other elements, the following merit a short description:—

Sulphur Chloride, S_2Cl_2.—On passing chlorine over melted sulphur, a chloride is formed, having the formula S_2Cl_2. This body is a volatile liquid, and may be condensed by collection in a receiver kept cool by a current of water. As thus prepared, the chloride contains an excess of chlorine, from which it is freed by redistillation from powdered sulphur. Sulphur chloride is a yellow liquid possessing a peculiar penetrating smell. It readily dissolves sulphur, and on contact with water yields hydrochloric and sulphurous acids. On passing chlorine into sulphur chloride at low temperatures, chlorides are formed which contain a higher proportion of chlorine. The formulæ of these are SCl_2 and SCl_4; they are both unstable and unimportant bodies.

Carbon Disulphide, CS_2.—This most important body is produced by the combustion of charcoal in sulphur vapour. On the small scale it may be prepared by attaching a retort to an iron tube loaded with charcoal and placed in a furnace. The further end of this tube is connected with a condensing worm, the end of which enters a receiver. The iron tube is made red-hot and the sulphur in the retort caused to boil, so that its vapour passes over the red-hot charcoal. Combination occurs according to the following equation:—

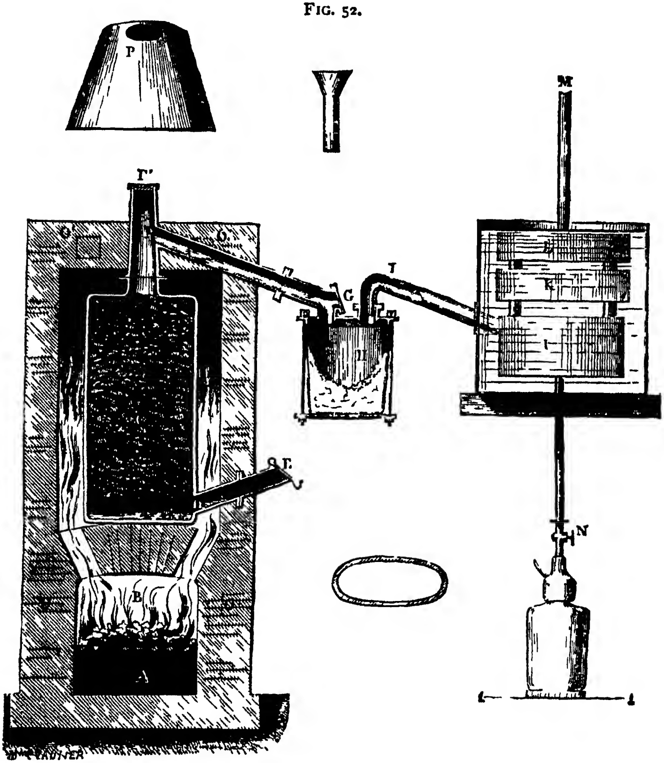
$$\underset{\text{Carbon.}}{C} + \underset{\text{Sulphur.}}{S_2} = \underset{\text{Carbon disulphide.}}{CS_2}.$$

The disulphide condenses to a volatile liquid in its passage through the condenser.

On the large scale carbon disulphide is prepared in an apparatus, one form of which is shown in fig. 52. The vessel C, in which the charcoal is heated, is about six feet high and constructed of cast iron. At the top is an opening, through which the charcoal is admitted. Towards the bottom is a tube, D,

fitted with a cover, E. This vessel is enclosed in brickwork, and having been charged with charcoal is raised to a red heat by the fire underneath. From time to time sulphur is added through the tube D; this volatilises, and its vapour passing up-

FIG. 52.



wards through the charcoal is converted into the disulphide. Through the tube F G the vapour passes into a receiver H, in which any solid impurities carried over mechanically are deposited. From this the vaporous disulphide passes through I into a series of condensing vessels J K L, enclosed in a tank of cold water, in which it is condensed to the liquid form. From these condensers the disulphide is drawn off by the tap N.

In its crude form carbon disulphide contains a considerable quantity of sulphur in solution; from this it is freed by redistillation.

Carbon disulphide is a colourless, mobile, and volatile liquid, of 1·272 specific gravity, which has a very high index of refraction, and is not miscible with water. It is very inflammable, and its vapour takes fire in air at a temperature of 149° C., burning with a blue flame, and yielding carbon and sulphur dioxides--

$$\underset{\text{Carbon disulphide.}}{CS_2} + \underset{\text{Oxygen.}}{3O_2} = \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Sulphur dioxide.}}{2SO_2}.$$

The commercial disulphide has a most offensive odour, due largely to impurities; but even when in a highly pure state the smell, though somewhat ethereal, is far from an agreeable one. The vapour is very poisonous, producing a train of unpleasant symptoms in those exposed to its influence. Its poisonous nature leads to its employment as a means of freeing grain, &c., from injurious insects. A small quantity is mixed with the grain in an airtight chamber, and the vapour kills both insects and their larvæ. On being freely exposed to the air the disulphide completely evaporates. Carbon disulphide acts as an antiseptic to meat, which may be preserved for long periods by enclosure in an airtight vessel with its vapour.

The value of carbon disulphide in the arts depends on its great solvent power for many substances; among these are sulphur, phosphorus, caoutchouc, fats and resins. In vulcanising india-rubber the crude caoutchouc is treated with a mixture of sulphur chloride and carbon disulphide, from which it abstracts the sulphur. As a fat-extractor, carbon disulphide is employed for removing fat in wool-cleaning processes, and also for extracting oil from crushed linseed and other oil sources.

Carbon disulphide is in composition analogous to the dioxide, and, like it, may also be viewed as the anhydride of a corresponding acid, the acid in this case being one in which oxygen is replaced by sulphur. The alkaline sulpho-carbonates are formed by treating the sulphite of the metal with carbon

disulphide. That of potassium has the following composition: K_2CS_3. From this body it is possible to obtain sulpho-carbonic acid, thus:—

K_2CS_3	+	$2HCl$	=	$2KCl$	+	H_2CS_3.
Potassium sulpho-carbonate.		Hydrochloric acid.		Potassium chloride.		Sulpho-carbonic acid.

CHAPTER XVII

OXIDES AND ACIDS OF SULPHUR

225. **Sulphur Oxides.**—Three oxides of sulphur are known:—

Sulphur sesquioxide, S_2O_3.
Sulphur dioxide or sulphurous anhydride, SO_2.
Sulphur trioxide or sulphuric anhydride, SO_3.

By the action of water we have:—

$SO_2 + H_2O = H_2SO_3$, Sulphurous acid.
$SO_3 + H_2O = H_2SO_4$, Sulphuric acid.

In addition, there are the following other oxyacids of sulphur:—

Disulphuric acid (Nordhausen sulphuric acid)	$H_2S_2O_7$.
Hyposulphurous acid (Hydrosulphurous acid)	H_2SO_2.
Thiosulphuric acid or Sulphosulphuric acid (Hyposulphurous acid)	$H_2S_2O_3$.
Dithionic acid.	$H_2S_2O_6$.
Trithionic acid	$H_2S_3O_6$.
Tetrathionic acid	$H_2S_4O_6$.
Pentathionic acid	$H_2S_5O_6$.

The lowest oxide of sulphur possesses little importance, and therefore may be passed over without further description.

Sulphur Dioxide.—Formula, SO_2. Molecular weight, 63·9. Density, 31·95. Specific gravity, 2·247. Melting-point, 76°. Boiling-point, 8° C.

226. **Occurrence.**—This compound is a gas at ordinary

temperatures, and is emitted in vast quantities from volcanoes. The student is already familiar with its preparation by the combustion of sulphur in oxygen.

227. Preparation.—When required for laboratory use it is prepared by the action of some deoxidising agent on sulphuric acid.

It has been already shown that zinc energetically displaces the hydrogen from sulphuric acid; but certain other metals, as copper, silver, and mercury, are without action, except on the application of heat, when chemical action ensues, which is probably represented by the following equation:—

$$\underset{\text{Copper.}}{Cu} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\textit{Nascent}\text{ hydrogen.}}{2H.}$$

At the high temperature the nascent hydrogen attacks a second molecule of sulphuric acid, thus:—

$$\underset{\text{Nascent hydrogen.}}{2H} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Sulphur dioxide.}}{SO_2.}$$

These successive steps in the reaction may be grouped together in one equation:—

$$\underset{\text{Copper.}}{Cu} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Sulphur dioxide.}}{SO_2.}$$

Sulphur dioxide may also be prepared from sulphuric acid by the action of charcoal; carbon dioxide, however, is also produced:—

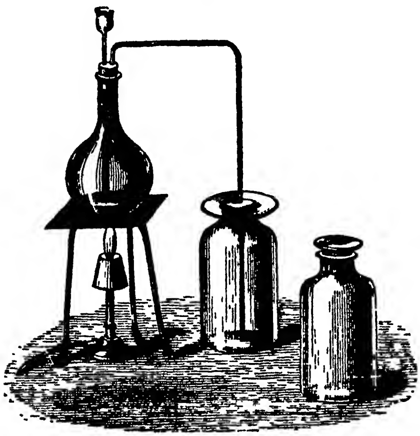
$$\underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Carbon.}}{C} = \underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{2H_2O.}$$

The gas being soluble in water must be collected by displacement or over mercury. For the purpose of preparing the gas, the apparatus shown in fig. 53 may be employed. About half an ounce of copper turnings or strips is placed in the flask, and then some three ounces of concentrated sulphuric acid. The flask is gently heated and the gas jars filled by displacement.

Sulphur dioxide is one of those gases which condense at a comparatively high temperature. It may be readily obtained in

the liquid form by passing the dried gas through a freezing mixture of ice and salt. An apparatus such as is shown in figure 54 is suitable for the purpose. A is the glass flask in which the gas is generated, after which it passes through the small wash-bottle B, containing concentrated sulphuric acid. On emerging from this it passes into a spiral glass or pewter worm, contained within a vessel C, containing a mixture of ice and salt. The condensed dioxide drops into a tube immersed within the beaker D, and also containing ice and salt.

FIG. 53.

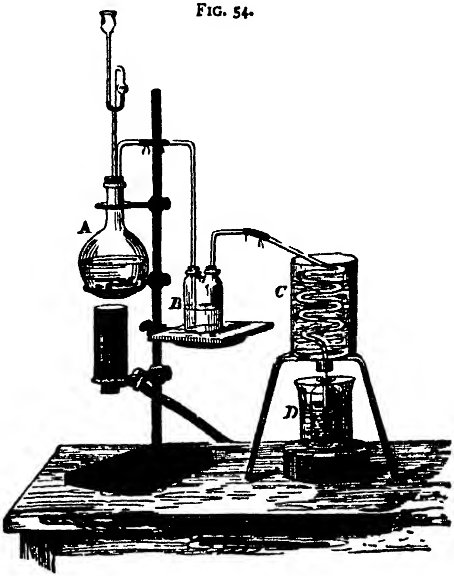


228. Manufacture.—For manufacturing purposes sulphur dioxide may be prepared by heating sulphuric acid with charcoal, or by roasting sulphur ore (pyrites) in a furnace, and thus oxidising the sulphur to dioxide.

229. Properties.—Sulphur dioxide is a colourless gas possessing a strong characteristic pungent odour; when diluted with air, coughing and sneezing are produced by it, while in a more concentrated form it causes suffocation. Sulphur dioxide is neither inflammable nor a supporter of combustion At $-8°$ C. it condenses to a liquid, which form it also assumes at 15° on being subjected to a pressure of 2·5 atmospheres (37·5 lbs. per square inch). Like other gases which readily condense, sulphur dioxide does not implicitly follow Boyle's law; the pressure being doubled, the volume contracts to less than one-half. It is probable that the molecules of all gases when near their condensing-point do not remain absolutely free from each other. Gases in that condition may be viewed as having aggregated groups of molecules floating about in them; an

increase in pressure increases the number of such groups and hence the volume diminishes in a quicker ratio than follows from Boyle's law.[1]

FIG. 54.



Sulphur dioxide is a powerful antiseptic and disinfectant ; it also possesses bleaching properties, which latter, however, are dependent on the presence of water.

Water at a temperature of 15° C. dissolves 47 volumes of sulphur dioxide, and thus produces a true though somewhat unstable acid—sulphurous acid, H_2SO_3. This acid has never been separated from excess of water, and is decomposed on boiling, as at that temperature the whole of the sulphur dioxide may be expelled from the water.

230. Industrial Applications.—Sulphur dioxide is used in enormous quantities for the preparation of sulphuric acid. It is also somewhat extensively used for bleaching purposes.

[1] Under such conditions, and for the same reasons, gases do not implicitly obey Avogadro's law, and also others to which they are subject when in the perfect gaseous state.

Bleaching Action.—If a bunch of moistened violets be placed in a jar containing sulphur dioxide the colour is rapidly discharged; the same reaction also occurs with many other vegetable colours. As a bleaching agent it differs remarkably from chlorine; it will be remembered that the latter decomposes water, seizing the hydrogen, and that the nascent oxygen destroys the colouring matter by change into bodies containing a large proportion of that element.

Colouring matters which have been acted on by chlorine are entirely destroyed, and cannot be reproduced; colours removed by sulphur dioxide are again restored either by its displacement by a stronger acid, as dilute sulphuric, or its neutralisation by combination with an alkali. Miller considers the acid to act by forming colourless compounds with the colouring matters. The action is also explained by stating that the colouring matters are reduced, the sulphurous acid being, in the presence of water, oxidised into sulphuric acid, with the liberation of nascent hydrogen, which latter acts as the reducing agent. It is difficult, however, with this assumption, to explain how the addition of either sulphuric acid or an alkali should again restore the colour, as neither of these bodies is an oxidising agent. Sulphur dioxide is used for the bleaching of articles, such as silk, straw, and wool, which would be injured by the action of chlorine. The goods to be bleached are moistened and hung in a chamber in which sulphur dioxide is formed by the burning of sulphur.

Antichlor.—Sulphur dioxide is used for the purpose of removing traces of chlorine from goods bleached by that agent; sulphuric and hydrochloric acids are formed by their mutual action, and may be afterwards removed by copious washing; more usually, however, the sodium salt of sulphurous acid is employed: this possesses the advantage that the alkaline base combines with the resulting acids and forms non-corrosive salts.

From its possessing this property, sodium sulphite is known commercially under the name of antichlor. Its action is represented in the following equation, where it is assumed that excess of the sulphite is used:—

$$\underset{\text{Sodium sulphite.}}{2Na_2SO_3} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Sulphur dioxide.}}{SO_2}.$$

Disinfectant Action.—In order to disinfect sick rooms after attacks of typhus fever and other contagious diseases, sulphur is burned in them, care being taken to close all crevices and openings into the room. The same treatment disinfects any clothing which may be contained in the chamber, and also destroys obnoxious insect life.

231. Composition.—This may be determined by burning a fragment of sulphur in oxygen in the same bulbed eudiometer as was described in paragraph 135, on the composition of carbon dioxide, and illustrated in fig. 36. The volume of the resultant gas is found to be the same as that of the oxygen before combustion. The molecule of sulphur dioxide is therefore shown to contain its own volume of oxygen.

232. Sulphurous Acid.—This acid is produced by passing sulphur dioxide into water, which latter remains in excess. Sulphurous acid turns litmus solution red and afterwards discharges the colour; it smells and tastes of sulphur dioxide. Sulphurous acid is dibasic and forms two series of salts called sulphites; thus, on the addition of barium chloride to sulphurous acid, the following reaction occurs:—

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + \underset{\text{Barium chloride.}}{BaCl_2} = \underset{\text{Barium sulphite.}}{BaSO_3} + \underset{\text{Hydrochloric acid.}}{2HCl}.$$

If the solution be rendered acid by treatment with hydrochloric acid previous to the addition of the barium chloride, no precipitate is formed. Any stronger acid, such as hydrochloric or sulphuric acid, decomposes the sulphites with evolution of sulphur dioxide.

$$\underset{\text{Sodium sulphite.}}{Na_2SO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Water.}}{H_2O}.$$

Sulphur Trioxide.—Formula, SO_3. Molecular weight, 79·86. Density, 39·93.

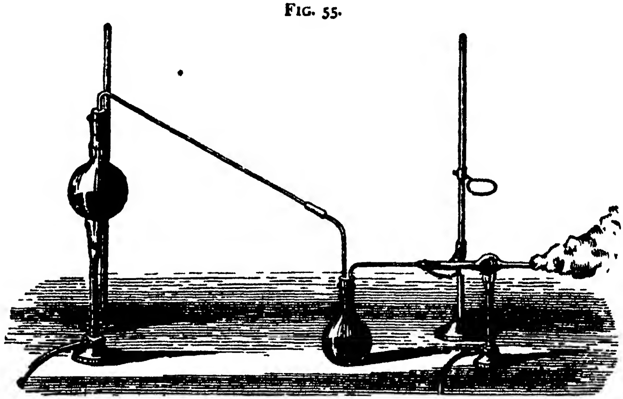
233. Preparation.—Sulphur does not readily combine with more than two atoms of oxygen; but by passing a mixture

of sulphur dioxide and oxygen over ignited spongy platinum, sulphur trioxide is produced :—

$$\underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Sulphur trioxide.}}{2SO_3}.$$

Instead of spongy platinum, platinised asbestos fibre may be employed. This consists of asbestos first dipped in a solution of platinum chloride, and dried, and then into one of ammonium chloride, dried and ignited. A thin coating of platinum is thus formed on each fibre. For experimental purposes, a four-ounce flask should be fitted up as a wash-bottle, and partly filled with saturated solution of sulphurous acid in water. To this is

FIG. 55.



attached an oxygen-generating flask, fig. 55, and to the other tube of the wash-bottle a bulb-tube of combustion-tubing. The bulb of this tube is filled with the platinised asbestos, under which a burner is placed so as to gently warm it. On now warming the oxygen-generating flask a current of oxygen is obtained; this, by passing through the wash-bottle, becomes mixed with sulphur dioxide, and so the two find their way into the bulb-tube, and there combine to form sulphur trioxide, which escapes from the apparatus as a cloud of dense white fumes.

Sulphur trioxide is also produced by the action of heat on Nordhausen sulphuric acid ; thus :—

$$\underset{\text{Nordhausen sulphuric acid.}}{H_2S_2O_7} = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Sulphur trioxide.}}{SO_3}.$$

234. Properties.—Sulphur trioxide when prepared with the absolute exclusion of water is obtained as a white silky-looking mass, which, according to Weber, when purified by repeated distillations in hermetically sealed tubes, is changed into a colourless liquid. It is devoid of all acid properties, and, in the solid form, may be rolled between the *dry* fingers without injury. By passage through a red-hot tube, it is separated into oxygen and sulphur dioxide :—

$$\underset{\text{Sulphur trioxide.}}{2SO_3} = \underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Oxygen.}}{O_2}.$$

Sulphur trioxide is very deliquescent, and when dropped into water, dissolves with a hissing noise and evolution of great heat, forming sulphuric acid :—

$$\underset{\text{Sulphur trioxide, or sulphuric anhydride.}}{SO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$

When the two are once united, their separation cannot be effected by heat alone ; for a temperature sufficiently high to dissociate them also decomposes sulphur trioxide into sulphur dioxide and oxygen.

Sulphuric Acid. — Formula, H_2SO_4. Molecular weight, 97·82. Specific gravity of liquid, 1·846. Melting-point, 10·5° C. Boiling-point, 338°.

235. Importance.—There is no other compound, with the exception of water, which is of such importance to the chemist as sulphuric acid. The frequency of its application to various purposes in the preceding chapters will have given the student some idea of its usefulness, and have rendered him familiar with its appearance, many of its properties, and its composition. It holds an equally important position in the chemical manufactures as in the laboratory. Its preparation is the starting-point in the manufacture of hydrochloric acid, sodium carbonate, nitric acid, and many other bodies of value in the arts.

236. Preparation.— Finely powdered sulphur, when moistened, is in part gradually oxidised into sulphuric acid; by prolonged boiling with nitric acid, the whole becomes oxidised.

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Nitric acid.}}{12HNO_3} = \underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Nitrogen peroxide.}}{12NO_2} + \underset{\text{Water.}}{4H_2O}.$$

Nitric acid has a similar action on some native sulphides. Sulphurous acid may be readily oxidised to sulphuric acid by the aid of oxidising agents, thus on adding a few drops of con centrated nitric acid to pure sulphurous acid in a test-tube and heating gently, oxidation occurs. On now adding to the liquid some hydrochloric acid and barium chloride, a white precipitate of barium sulphate, insoluble in acids, is formed. The change to sulphuric acid may be thus represented :—

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Nitrogen peroxide.}}{2NO_2} + \underset{\text{Water.}}{H_2O}.$$

237. Manufacture.— Sulphuric acid is always manufactured on the large scale by the oxidation of sulphur dioxide in the presence of water. The reactions involved are of great interest. The vapour of nitric acid is passed into a chamber with sulphur dioxide, air, and steam. As previously shown, the nitric acid is deoxidised into nitrogen peroxide, with the formation of sulphuric acid. A reaction now ensues between the nitrogen peroxide and some more sulphur dioxide, more sulphuric acid is produced, and the nitrogen peroxide is reduced to nitrogen dioxide. The student will remember that in the presence of air this colourless gas is immediately changed into the ruddy fumes of the trioxide and peroxide. Thus, higher oxides of nitrogen are again formed, and are capable of oxidising more sulphur dioxide. Sulphur dioxide does not readily combine with oxygen, but is immediately oxidised by nitrogen peroxide. The dioxide unites directly with oxygen, and so acts as a carrier of oxygen from the air to the sulphur dioxide. A small amount of nitric acid is thus theoretically capable of producing an indefinite quantity of sulphuric acid. The whole series of changes is shown in the following equations :—

$$\underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Nitrogen peroxide.}}{2NO_2}.$$

$$\underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Nitrogen peroxide.}}{NO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Nitric oxide.}}{NO}.$$

$$\underset{\text{Nitric oxide.}}{8NO} + \underset{\text{Oxygen.}}{3O_2} = \underset{\text{Nitrogen trioxide.}}{2N_2O_3} + \underset{\text{Nitrogen peroxide.}}{4NO_2}.$$

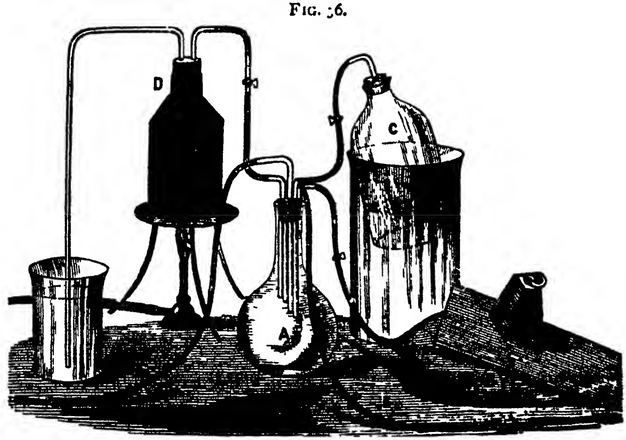
The proportions of higher oxides are not constant, but depend on the quantity of oxygen present.

The above equations represent, in the simplest form, the action which takes place. In the absence of water a peculiar crystalline compound is produced, which may be represented by the formula $S_2O_5(NO_2)_2$. This is immediately decomposed by water, with the formation of sulphuric acid and liberation of nitrogen trioxide:—

$$\underset{\text{Crystalline compound.}}{S_2O_5(NO_2)_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Nitrogen trioxide.}}{N_2O_3}.$$

On the small scale, these reactions may be watched by fitting up and employing the following apparatus, fig. 56. A is

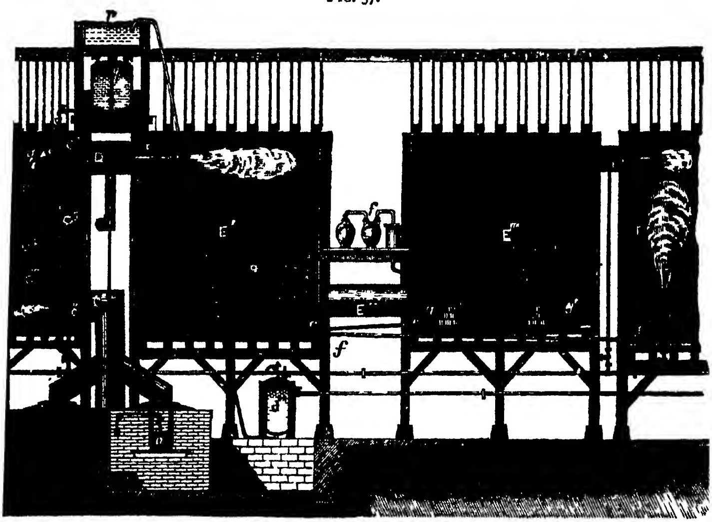
FIG. 56.



a large flask, to which is fitted a cork bored for five tubes. (This flask A may be advantageously replaced by a glass globe of the same size, fitted with three tubulures; through two of

these, corks are passed, bored for two tubes each, while the third tubulure has a single tube passed through its cork.) Sulphur dioxide is stored in the bladder or india-rubber gas-bag, B; the gas jar C is inverted in a large beaker of water, and serves as a gasholder for nitric oxide. Air or oxygen is conveyed by the tube E from a gas-bag. In a flask D, water is kept boiling, in order to supply steam when required. The last tube, F, is for the escape of waste gases; the whole of the tubes are controlled by screw-taps. The flask being thoroughly

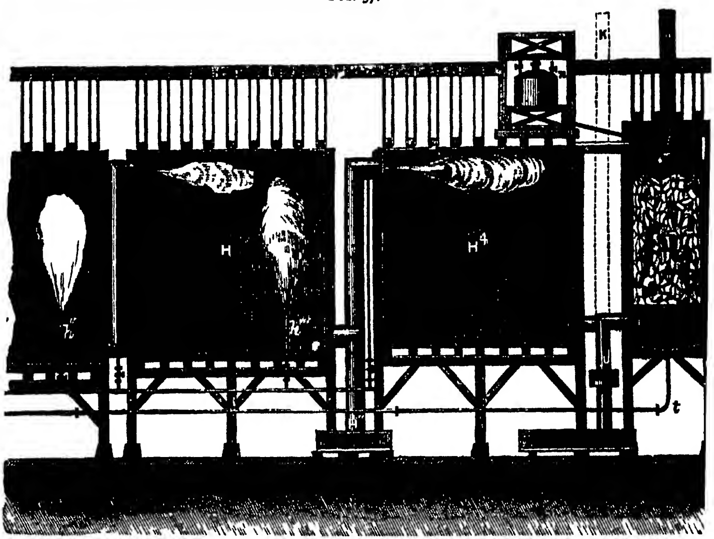
FIG. 57.



dry, nitric oxide is admitted, when ruddy fumes are immediately formed. Sulphur dioxide is next allowed to pass into the flask, and the ruddy fumes at first formed disappear. A white crystalline deposit is now observed to form on the sides of the flask. With the admission of more air, nitric oxide and sulphur dioxide, the formation of this crystalline deposit continues. On shutting off the whole of these and admitting a small quantity of steam, the crystalline compound disappears, and nitrous fumes are once more liberated. If the admission of steam be continued in very small quantity, and then sulphur

dioxide is introduced, the ruddy tint of the nitrogen peroxide quickly disappears. If the sulphur dioxide be then shut off and air admitted instead, the nitric oxide is once more oxidised, as demonstrated by the reappearance of the ruddy hue. This cycle of changes may be caused to occur several times; in practice they cannot continue indefinitely because the nitrogen of the air gradually washes the whole of the other gases out of the flask through the escape-tube. Consequently, to replenish this waste, nitric oxide must be continuously added in small

FIG. 57.



quantity. At the conclusion of the experiment, a quantity of sulphuric acid is found collected at the bottom of the flask.

In the manufacture of sulphuric acid, the sulphur dioxide may be produced by burning sulphur or by roasting sulphur ore (pyrites) in a suitable furnace. In this way a mixture of sulphur dioxide and air is formed. The reaction between the various bodies occurs in large chambers made of timber framing and lined with sheet lead, the joints being made air-tight by soldering the edges of the lead together by the oxyhydrogen

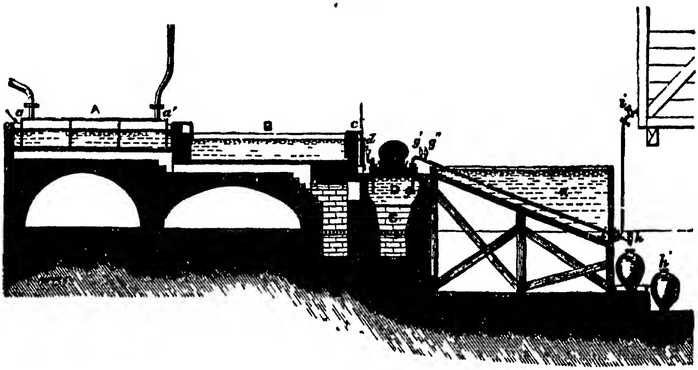
blowpipe. Fig. 57 is a sectional elevation through a sulphuric acid plant. A is one of a pair of furnaces arranged for the burning of sulphur. The mixed gases from these furnaces pass through the tubes B B into a leaden chamber C C^7, fitted with a number of baffle shelves. These provide for thorough admixture of the gases, which are also moistened by the introduction of a jet of steam from c''. The whole series of gases find their way through D into E′. To stimulate the draught a current of steam, E, is also admitted at this point. Through the pipe E″ the gases pass into the chamber E‴. Into this chamber nitric acid is admitted from the stone-ware jars *f*, and flows over the conical arrangements, *g g′*, in order to expose as much surface as possible. Here the characteristic sulphuric acid reaction occurs, and results in the production of sulphuric acid containing large quantities of nitric acid and oxides of nitrogen; this acid is allowed to flow back through *e′ e* into the first chamber E′, where it meets the fresh mixture of gases emerging from the generating furnaces. The still gaseous products from E‴ are conveyed by E^4 into the chamber F; this chamber, together with H and H^4, are fitted with steam jets and serve to allow the completion of the reactions by which the dioxide is oxidised to sulphuric acid. At the end is a tower, J J′, by which the nitrous fumes remaining are dissolved by a slowly descending stream of concentrated sulphuric acid, in which they are very soluble. The acid condenses on the floors of the various chambers and is drawn off through pipes arranged for that purpose.

This is merely one arrangement of such a manufacturing plant; it is susceptible of numerous and diversified modifications. One plan frequently adopted is to place the vessel for the evaporisation of the nitric acid as close as possible to the main flues B B; a small steady stream is allowed to flow in and is evaporated by the heat of the furnace gases. It then passes over as vapour with the other gases into the chamber. The solution of nitrous fumes in sulphuric acid is used over again as a source of nitrogen oxides, thus reducing the actual nitric acid waste to a narrow limit.

The acid from the bottom of the chambers, known commercially as chamber acid, has a specific gravity of about 1·55,

and contains about 64 per cent. of sulphuric acid mixed with 36 per cent. of water. It is not advisable to allow it to become more concentrated, as then it would dissolve considerable quantities of the oxides of nitrogen. Chamber acid is sufficiently strong for many technical purposes, but for others it must be further concentrated. This is effected by evaporation in leaden pans until the acid acquires a density of 1·75, after which the further concentration must be performed in vessels of either glass or platinum until a density of 1·842 is attained. (The acid of greater strength than 1·75 commences to rapidly attack lead.) A concentrating plant is shown in fig. 58: A

FIG. 58.



and B are open leaden pans in which the first concentration is performed, these pans being heated by the hot air from the furnace C. At *d* the concentrated acid, 1·75, is allowed to run into the platinum still D, from which, as it acquires sufficient concentration (to sp. gr. 1·842) it is syphoned off through the pipe *g h*, running through the cold water tank K. The steam from this still at first consists of little but water, but as the acid becomes more concentrated, a stronger acid distils over, which can be preserved and returned to the evaporating pans.

The acid of strength 1·75 constitutes the 'brown acid' of commerce; that of 1·842 density is known commercially as 'oil of vitriol.'

238. Properties.—Sulphuric acid in the pure state is a colourless, odourless liquid of oily consistency. It has a specific gravity of 1·842, but, like other acids described, the specific gravity diminishes with the degree of concentration. The following table gives the strength of pure sulphuric acid of various densities.

Density	Sulphuric acid, in 100 parts by weight	Density	Sulphuric acid, in 100 parts by weight
1·000	0·0	1·332	43·0
1·007	1·9	1·357	45·5
1·029	4·8	1·383	48·3
1·045	6·8	1·410	51·2
1·060	8·8	1·439	54·0
1·075	10·8	1·468	56·9
1·091	13·0	1·498	59·6
1·108	15·2	1·530	62·5
1·125	17·3	1·563	65·5
1·142	19·6	1·597	68·6
1·162	22·2	1·634	71·6
1·180	24·5	1·671	74·7
1·200	27·1	1·711	78·1
1·220	29·6	1·753	81·7
1·241	32·2	1·796	86·5
1·263	34·7	1·819	89·7
1·285	37·4	1·842	100·0
1·308	40·2	—	—

Sulphuric acid has a very great attraction for water, with which it forms definite compounds; the union of the two is attended with evolution of great heat and diminution in volume. In consequence it is necessary to use caution in mixing the two; the acid must be poured very gradually into the water, and not the water into the acid. Sulphuric acid attracts moisture from the air with great avidity, so much so that if the concentrated acid be exposed in an open dish it increases rapidly in volume from absorption of moisture. If the bulb of a thermometer be dipped in sulphuric acid and then held in a horizontal position so as to prevent the acid dropping off, the quantity can be seen within two or three minutes to visibly increase; at the same time the temperature of the thermometer rises. This power of attracting moisture leads sulphuric acid to be largely employed in the laboratory as a drying agent, and

for many purposes where the absorption of water is necessary. Owing to this affinity for water, sulphuric acid acts as a powerful caustic, and attacks and decomposes most organic bodies, assimilating the elements of water, and setting free the carbon and other constituents in various forms. Thus, as has been already described, sulphuric acid decomposes oxalic acid and other bodies, with the liberation of oxides of carbon. Fragments of wood or straw give the acid a brown colour, due to the carbonaceous compounds liberated on their being charred by the acid. Sugar and other highly carbonaceous bodies are violently attacked by sulphuric acid; the mixture froths up, leaving a black mass of impure carbon. At the same time a portion of the sulphuric acid is reduced to sulphur dioxide.

The high temperature of the boiling-point renders the acid specially suitable for the preparation of the more volatile acids—as nitric acid—from their salts; any excess of sulphuric acid, and the resultant sulphate formed, being non-volatile at the temperature at which nitric acid boils, are thus easily separated.

Sulphuric acid, being a dibasic acid, forms two well-marked series of salts, the one of which is normal; the other, still containing half the hydrogen, is acid. With the exception of a few basic salts, the sulphates are mostly soluble in water. The insoluble sulphates, among which must be included those of lead, barium, and strontium, are insoluble not only in water but all acids.

At a white heat the acid is decomposed into water, sulphur dioxide, and oxygen.

239. Industrial Applications.—Sulphuric acid is so widely employed in chemical and other manufactures that the extent of its use has been taken as the measure of the country's general commercial prosperity.

Sulphuric acid is largely employed in the preparation of other acids, as nitric and hydrochloric acids; also in the preparation of the sulphates, and for the production of an electric current in voltaic batteries.

In metallurgic operations sulphuric acid is used for cleaning

the surface of iron and copper plates, as a preliminary to their being coated with other metals, as tin or zinc.

Sulphuric acid is used in the preparation and treatment of ether and many other organic bodies.

It is also extensively employed in the preparation of bones and other phosphatic substances for manure, producing by its action a soluble calcium phosphate.

240. Nordhausen Sulphuric Acid, $H_2S_2O_7$.—Nordhausen sulphuric acid may be looked on as a compound of a molecule of ordinary sulphuric acid with a molecule of sulphur trioxide: it is named after a town in Saxony, where it is prepared in large quantities by first drying ferrous sulphate, $FeSO_4,7H_2O$, and at a stronger heat decomposing it. The act of drying is accompanied by an oxidation of the ferrous sulphate to basic ferric sulphate, $Fe_2S_2O_9$. Supposing the whole of the water to have been thus driven off, the act of heating would result in the following change:—

$$\underset{\text{Basic ferric sulphate.}}{Fe_2SO_9} = \underset{\text{Sulphur dioxide.}}{2SO_3} + \underset{\text{Ferric oxide.}}{Fe_2O_3}.$$

But in the presence of small quantities of moisture a portion of the anhydride is converted into sulphuric acid, and this dissolves another molecule of the trioxide, $H_2S_2O_7$ being equivalent to H_2SO_4,SO_3. Nordhausen or disulphuric acid is an oily fuming liquid, having a density of about 1·9. The molecule of sulphur trioxide, in Nordhausen sulphuric acid, being only held in feeble combination, is readily driven off by heat.

Nordhausen sulphuric acid forms a stable series of salts, whose formulæ correspond with that of the acid; thus the sodium salt is represented by $Na_2S_2O_7$.

241. Hyposulphurous Acid, H_2SO_2.—On its discovery this body was termed *hydrosulphurous* acid, because the name 'hyposulphurous' had already been given to another acid. The formula shows this body to rightfully claim the name hyposulphurous acid, it having one atom less oxygen than has sulphurous acid. The zinc salt of this acid is obtained as a

yellow liquid on dissolving zinc in sulphurous acid; no hydrogen is evolved, and the following reaction occurs:—

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulphurous acid.}}{H_2SO_3} = \underset{\text{Zinc hyposulphite.}}{ZnSO_2} + \underset{\text{Water.}}{H_2O.}$$

The hyposulphites are very unstable salts, combining with oxygen with great avidity, and thus exercising great reducing power. The free acid is even more unstable than the salts.

242. Thiosulphuric or Sulphosulphuric Acid, $H_2S_2O_3$.—Prior to the discovery of the acid H_2SO_2, thiosulphuric acid was known as hyposulphurous acid; but this name is now replaced by that which heads this paragraph. The prefix 'thio' is derived from the Greek for sulphur; the two names thiosulphuric and sulphosulphuric are therefore identical in meaning. This acid may be viewed as sulphuric acid in which one of the oxygen atoms is replaced by dyad sulphur; it is an intermediate body between the oxy-acids and the sulpho-acids, in which sulphur entirely replaces oxygen, fulfilling the same functions. (See paragraph 224 on carbon di-sulphide.) The probable constitution of thiosulphuric acid, compared with that of sulphuric acid, is shown in the appended graphic formulæ. To distinguish the hexad or grouping sulphur atom from the merely dyad or oxygen-replacing one, the formula is sometimes written H_2SSO_3.

$$\underset{\text{Sulphuric acid.}}{\begin{matrix} O \\ O \end{matrix}\!\!\gg\! S \!\begin{matrix} -O-H \\ -O-H \end{matrix}} \qquad \underset{\text{Thiosulphuric acid.}}{\begin{matrix} S \\ O \end{matrix}\!\!\gg\! S \!\begin{matrix} -O-H \\ -O-H \end{matrix}}$$

The most important compound of thiosulphuric acid is sodium thiosulphate, $Na_2S_2O_3,5H_2O$, known commercially as hyposulphite of soda. This body may be prepared by digesting a solution of sodium sulphite with sulphur in a fine state of division, when the sulphite is 'sulphurised' into the thiosulphate:—

$$\underset{\text{Sodium sulphite.}}{Na_2SO_3} + \underset{\text{Sulphur.}}{S} = \underset{\text{Sodium thiosulphate.}}{Na_2S_2O_3.}$$

This salt occurs in large colourless crystals, easily soluble in water, and possessing the property, when in solution, of dissolving the haloid salts of silver (chloride, AgCl; bromide,

AgBr, and iodide, AgI). It is in consequence largely used in photography for dissolving out these salts from photographs, negative or positive, after development.

243. Thionic Acids.—These bodies are of little importance, and will not receive further reference here.

CHAPTER XVIII

THE HALOGENS

Bromine, Iodine, and Fluorine

244. The Halogens.—The three elements, bromine, iodine, and fluorine, together with chlorine already described, constitute the group known as the 'halogens.' As most acids are oxy-acids, their corresponding salts must contain oxygen; but the halogens yield salts which are binary compounds by direct union with the metals. These salts, from their similarity to sea-salt, are termed 'haloid' salts, and hence the name halogens given to the elements from which, by combination with the metals, they are produced.

The relations of the members of this group to each other are very interesting, but may be studied much better after some knowledge is gained of the elements themselves.

Bromine. — Symbol, Br. Atomic weight, 79·75. Density, 79·75. Specific gravity as gas, 5·51; as liquid, 3·18. Molecular weight, Br_2, 159·5. Melting-point, − 24·5°. Boiling-point, 59·5°C.

245. Occurrence.—Like chlorine, this element is never found free in nature, but in combination with other elements, usually either sodium, potassium, or magnesium. Balard, in 1826, discovered bromine in the mineral matter contained in sea-water; it also occurs in certain mineral deposits, particularly in the vast salt deposits of Stassfurt, in Germany.

246. Preparation.—Bromine is prepared from the soluble

bromides by the action of manganese dioxide and sulphuric acid in a manner precisely analogous to that employed for the production of chlorine from sodium chloride by the same reagents. Finely powdered potassium bromide and manganese dioxide are mixed together, placed in a flask or retort, and sulphuric acid added. On being gently heated, dark red vapours are evolved, which condense to a deep red liquid, according to the equation

$$\underset{\substack{\text{Potassium}\\\text{bromide.}}}{2KBr} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2} =$$

$$\underset{\substack{\text{Hydrogen}\\\text{potassium sulphate.}}}{2KHSO_4} + \underset{\substack{\text{Manganese}\\\text{sulphate.}}}{MnSO_4} + \underset{\text{Bromide.}}{Br_2} + \underset{\text{Water.}}{2H_2O.}$$

247. Extraction.—The first step in the extraction of bromine is to separate the bromides from the chlorides with which they are in nature associated. The solid salts are dissolved, and then concentrated by evaporation; the chlorides, being less soluble, first crystallise out and leave a mother-liquor in which the bromides predominate. Owing to the bitter taste possessed by this liquid, it has received the name of *bittern*. If chlorine be passed through this solution, bromine is liberated according to the following equation:—

$$\underset{\substack{\text{Potassium}\\\text{bromide.}}}{2KBr} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{2KCl} + \underset{\text{Bromine.}}{Br_2.}$$

The bromine at first set free imparts a reddish-brown colour to the solution. On shaking this with ether the bromine is dissolved, and its ethereal solution rises to the surface, and may be poured off from the watery layer underneath. On this ethereal solution being treated with potassium hydrate, its red colour disappears, bromide and bromate of potassium being formed:—

$$\underset{\text{Bromine.}}{Br_2} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{6KHO} = \underset{\substack{\text{Potassium}\\\text{bromide.}}}{5KBr} + \underset{\substack{\text{Potassium}\\\text{bromate.}}}{KBrO_3} + \underset{\text{Water.}}{3H_2O.}$$

The ether may be distilled off and re-collected; the solid residue of bromide and bromate is ignited in ordered to decom-

pose the bromate, which splits up into bromide and oxygen in the same manner as does potassium chlorate. In this way potassium bromide is obtained, from which the bromine may again be liberated by gently heating the bromide with manganese dioxide and sulphuric acid in the manner just described.

At times the mother-liquor, instead of being treated with chlorine, is evaporated down to dryness, and the residue mixed direct with sulphuric acid and manganese dioxide; but in this case, as chlorides are always present in the mother-liquor, chlorine is evolved as well as bromine. As these two elements readily combine to produce a chloride of bromine, the bromine thus prepared is more or less contaminated with this compound. The bromine may be purified by redistillation with potassium bromide, when the chlorine present liberates from the bromide an equivalent of bromine, itself combining with the potassium.

248. Properties.—Bromine at ordinary temperatures is a dark red liquid, so heavy that glass floats readily in it. It gives off a deep reddish-brown vapour, with a smell resembling that of chlorine, only far more intense. Bromine freezes at $-22°$ C. and boils at $63°$ C. Water dissolves about 3 per cent. of bromine; the solution possesses bleaching powers, but not to such an extent as chlorine. In this, as in its other reactions, bromine and chlorine closely resemble each other; but bromine is the less active of the two, and is displaced from its compounds by chlorine.

Bromine is not inflammable, neither does it support the combustion of a candle, but phosphorus combines directly with it, as with chlorine.

Bromine unites with hydrogen to form a colourless fuming gas, hydrobromic acid, HBr, very similar in character to hydrochloric acid.

Bromine vapour closely resembles nitrogen peroxide in appearance: the following tests distinguish the one from the other. On shaking with a small quantity of ether, bromine is dissolved, and imparts its characteristic tint to the ether; nitrogen peroxide does not affect the colour. If to the bottle or jar containing bromine vapour a solution of potassium hydrate be added, the

colour is removed. If this solution be very slightly acidulated by the addition of dilute nitric acid, and then silver nitrate added, there is a precipitate of silver bromide. Similar treatment causes no precipitate with nitrogen peroxide.

249. **Industrial Applications.**—Bromine is largely used in the preparation of bromides, and is also employed to some extent as a disinfectant.

Hydrobromic Acid.—Formula, HBr. Molecular weight, 80·75. Density, 40·37.

250. **Preparation.**—Hydrogen and bromine cannot readily be made to unite directly with each other; thus the passage of an electric spark through a mixture of bromine vapour and hydrogen, does not result in combination. Neither can hydrobromic acid be obtained by the decomposition of a bromide by sulphuric acid, as is done with a chloride, because a large proportion of the liberated hydrobromic acid is decomposed into free bromine, with the reduction of the sulphuric to sulphurous acid.

$$\underset{\text{Hydrobromic acid.}}{2HBr} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Bromine.}}{Br_2} + \underset{\text{Water:}}{2H_2O} + \underset{\text{Sulphur dioxide.}}{SO_2}.$$

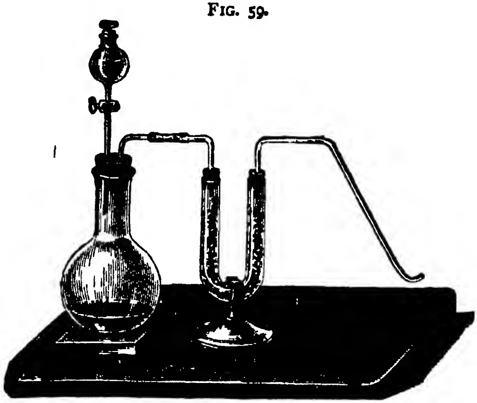
Hydrobromic acid may be prepared by distilling a bromide with phosphoric acid, or more conveniently by the action of water on phosphorous bromide, when the following reaction occurs:

$$\underset{\text{Phosphorous bromide.}}{PBr_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphorous acid.}}{H_2PHO_3} + \underset{\text{Hydrobromic acid.}}{3HBr}.$$

The preparation is effected in the apparatus shown in fig. 59, which consists of a large glass flask arranged with a delivery-tube, and bulb-funnel fitted with a stopper and stopcock. To the delivery-tube is attached a U-tube. A mixture of one part of amorphous phosphorus with two parts of water is placed in the flask; ten parts of bromine are poured into the funnel. The U-tube is charged with fragments of glass and ordinary phosphorus. By means of the stopcock the

bromine is admitted drop by drop, phosphorous bromide being formed and at once decomposed by the water. The hydro-

FIG. 59.



bromic acid which passes over is freed from any traces of bromine by the phosphorus in the U-tube.

251. Properties.—Hydrobromic acid is a colourless gas, fuming on exposure to air, and possessing a sharp pungent odour. It is not inflammable, neither is it a supporter of combustion. The gas is very soluble in water, yielding a colourless, fuming solution, of a specific gravity of 1·515, containing 50 per cent. of the acid HBr. Hydrobromic acid is decomposed by chlorine, with the liberation of free bromine. Hydrobromic acid is monobasic, and by its action on bases a series of salts, termed bromides, are formed. Most of the bromides are soluble in water, the exceptions being those of silver and lead. The former salt is extensively employed in the preparation of photographic sensitive plates. All the bromides are decomposed by chlorine, with the liberation of free bromine.

252. Bromic Acid, $HBrO_3$.—By a reaction similar to that employed for the production of potassium chlorate, potassium bromate, $KBrO_3$, may be obtained. It is separated from the simultaneously produced bromide by crystallisation. The

bromates, like the chlorates, are decomposed by heat, with the evolution of oxygen. The acid may be prepared by adding dilute sulphuric acid to a solution of barium bromate, so long as a precipitate is produced.

$$\underset{\text{Barium bromate.}}{Ba(BrO_3)_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Bromic acid.}}{2HBrO_3} + \underset{\text{Barium sulphate.}}{BaSO_4}.$$

In this manner a liquid is obtained which gives a strongly acid reaction, and at 100° C. is decomposed, with the liberation of free bromine and oxygen.

Iodine.—Symbol, I. Atomic weight, 126·53. Density, 126.53. Specific gravity as gas, 8·74; as solid, 4·95. Molecular weight, I_2, 253·06.

253. **Occurrence.**—Iodine, as well as bromine and chlorine, is found in sea-water, but in much smaller quantities. There are certain varieties of sea-weed which absorb the iodides and store them up in their tissues; from these the iodine of commerce is procured.

254. **Preparation.**—Iodine may be prepared from an iodide, as potassium iodide, by heating with manganese dioxide and sulphuric acid, when iodine is liberated, according to the equation :—

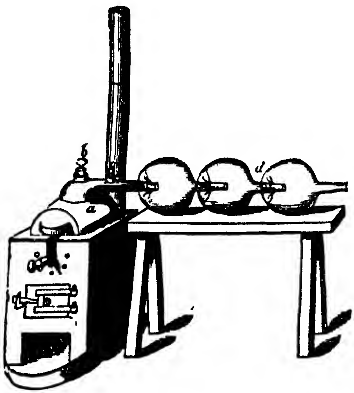
$$\underset{\text{Sodium iodide.}}{2NaI} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Manganese dioxide.}}{MnO_2} =$$

$$\underset{\substack{\text{Hydrogen}\\ \text{sodium sulphate.}}}{2NaHSO_4} + \underset{\substack{\text{Manganese}\\ \text{sulphate.}}}{MnSO_4} + \underset{\text{Iodine}}{I_2} + \underset{\text{Water.}}{2H_2O}.$$

255. **Extraction.**—Such sea-weeds as are sufficiently rich in iodides are dried and then burned; the ashes constitute the substance known as kelp. A preferable method is to employ only sufficient heat to carbonise the sea-weed, as with a high temperature, especially when prolonged, a quantity of the sodium iodide present is lost through volatilisation. The kelp, or carbonised sea-weed, is next treated with water (lixiviated), in order to dissolve out the sodium iodide, which is also accompanied with the bromide, chloride, and other impurities. It is

freed as far as possible from these by evaporation and crystallisation, after which remains a liquid containing sodium bromide, iodide, sulphide, thiosulphate and carbonate. To this liquid sulphuric acid is added, and the carbonates and sulphides decomposed; when it no longer smells of sulphuretted hydrogen, the liquid is drawn off and transferred to a cylindrical leaden still, *a*, fig. 60, to the stoppered head, *b*, of which is attached a series of large glass or stoneware receivers, *d*, *d*. The still is gently heated by means of a furnace and sand-bath, and then manganese dioxide is added in small quantities at a time; purple vapours of iodine distil over and condense within the receivers. By careful regulation of the quantity of manganese dioxide and temperature (which must not be allowed to rise too high), the greater part of the iodine distils over before the bromides are decomposed. At a higher temperature, with the addition of more dioxide, bromine distils over and is collected in a series of Woulffe's bottles. The iodine is purified by re-distillation.

FIG. 60.



It should be observed that chlorine, bromine, and iodine are liberated from the chlorides, bromides, and iodides by a precisely similar reaction.

256. Properties.—Iodine is, at ordinary temperatures, a dark-coloured (blue-black) solid, which gives off small quantities of vapour of a splendid violet tint. It may be obtained in well-defined crystals, and has a lustre almost metallic in character. At 115° C. iodine melts, and boils at a temperature of 200°. The violet tint of the vapour is then so dark as to appear almost black. The vapour possesses an odour resembling that

of chlorine, which odour may be distinguished on smelling the substances at ordinary temperatures. Iodine is slightly soluble in water, to which it imparts a light sherry tint; it is much more soluble in solutions of potassium iodide, and also in alcohol and ether. All these solutions are brown in colour. Iodine also dissolves in carbon disulphide, to which it imparts a violet tint resembling that of its vapour.

In chemical reactions iodine closely resembles bromine and chlorine, but is less active than these elements; consequently iodine may be liberated from the iodides by the addition of either bromine or chlorine. Iodine vapour is not inflammable, neither does it support combustion. Phosphorus, however, immediately takes fire on coming in contact with iodine. Iron and other metals are attacked, when placed in contact with this element, with the formation of iodides. Iodine possesses very feeble bleaching properties.

Iodine is characterised by yielding a most remarkable reaction with starch. The addition of a minute trace of free iodine colours starch solution a deep blue. The colour vanishes on boiling, but reappears as the liquid cools. Iodine when in a state of combination does not give this reaction; thus no colouration is produced on adding potassium iodide solution to starch paste, but if a few drops of either bromine-water or chlorine-water be added, iodine is liberated and immediately strikes the characteristic blue tint with the starch. This reaction forms a most useful test both for free iodine and starch. Bromine stains starch paste a deep yellow tint, while chlorine is without action.

257. Industrial Applications.—Iodine is largely used in medicine and in the preparation of a number of pharmaceutical compounds. In the form of potassium iodide it is extensively employed in photography. In the preparation of many organic compounds iodine is almost a necessity, and receives commercial application in the manufacture of certain aniline dyes.

Hydriodic Acid.—Formula, HI. Molecular weight, 127·53. Density, 63·76.

258. Preparation.—At a red heat hydrogen and iodine can be caused to combine to produce hydriodic acid. The acid is also liberated when potassium iodide is treated with sulphuric acid; it is, however, in great part at once decomposed with the liberation of free iodine and the reduction of sulphuric to sulphurous acid. It may be prepared in considerable quantity by the mutual action, at a gentle heat, of potassium iodide, iodine, and phosphorus on each other in the presence of water. Iodide of phosphorus is formed and decomposed by the water into phosphoric and hydriodic acids. The phosphoric acid liberates some more hydriodic acid from the potassium iodide present. The following equation represents the result of the reaction:—

$$8KI + 10I_2 + P_4 + 16H_2O = 4K_2HPO_4 + 28HI.$$

$8KI$	$10I_2$	P_4	$16H_2O$	$4K_2HPO_4$	$28HI$
Potassium. iodide.	Iodine.	Phosphorus.	Water.	Hydric dipotassic phosphate.	Hydriodic acid.

Hydriodic acid may readily be obtained in dilute solution by passing sulphuretted hydrogen through water containing iodine in suspension, when the following reaction occurs:—

$$SH_2 + I_2 = S + 2HI.$$

SH_2	I_2	S	$2HI$
Sulpuretted hydrogen	Iodine.	Sulphur.	Hydriodic acid.

The sulphur may readily be removed by filtration.

259. Properties.—Hydriodic acid is a colourless fuming gas, very similar in general properties and appearance to the hydrogen compounds of bromine and chlorine. It is neither inflammable nor a supporter of combustion; at a red heat it is partly decomposed into free hydrogen and iodine. The gas is very soluble in water, and forms a solution, which at 15° C. has a density of 1·70, and contains 52 per cent. of HI. The acid readily dissolves iodine, forming a dark brown solution. Its decomposition is immediately effected by either chlorine or bromine, and is also produced by nitric acid and other oxidising agents—

$$2HNO_3 + 2HI = 2NO_2 + 2H_2O + I_2.$$

$2HNO_3$	$2HI$	$2NO_2$	$2H_2O$	I_2
Nitric acid.	Hydriodic acid.	Nitrogen peroxide.	Water.	Iodine.

Hydriodic acid is a powerful acid, dissolving zinc, with the evolution of hydrogen ; it is monobasic, and forms a series of salts termed iodides. The greater number of the iodides are soluble, those of silver and lead being exceptions. Potassium iodide is a most valuable medicinal agent ; silver iodide has most important photographic applications.

260. Iodic Acid, HIO_3.—On heating iodine with concentrated nitric acid the following reaction occurs :—

$$\underset{\text{Iodine.}}{8I_2} + \underset{\text{Nitric acid.}}{10HNO_3} = \underset{\text{Iodic acid.}}{6HIO_3} + \underset{\text{Nitric oxide.}}{10NO} + \underset{\text{Water.}}{2H_2O.}$$

The resultant solution is heated to 200° ; and at this temperature any remaining traces of nitric acid are driven off and the iodic acid is decomposed, with the formation of iodic anhydride, I_2O_5 :—

$$\underset{\text{Iodic acid.}}{2HIO_3} = \underset{\text{Iodic anhydride.}}{I_2O_5} + \underset{\text{Water.}}{H_2O.}$$

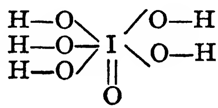
Iodic anhydride is a white powder, which readily dissolves in water, forming a thick syrupy liquid, from which crystals of iodic acid are deposited.

The formula HIO_3 is similar to those of chloric and bromic acids, but iodic acid forms a series of hydric alkaline salts, and consequently its formula is at times written $H_2I_2O_6$. This acid is colourless and odourless, and has a sour taste. Iodic acid differs considerably in properties from chloric and bromic acids, which are unstable bodies, and have no corresponding anhydrides. The iodic anhydride is, on the other hand, a very stable body, which requires a temperature of 371° C. to effect its decomposition into iodine and oxygen. The iodates are decomposed on the application of heat, yielding in the case of those of the alkali metals, iodides and free oxygen. The iodates of other metals evolve both iodine and oxygen, and leave either an oxide or the metal in the free state.

261. Periodic Acid, HIO_4.—This acid is unknown in the anhydrous condition, always being combined with two molecules of water, which is expressed by the formula H_5IO_6, or $HIO_4,2H_2O$. This acid is formed by the action of iodine on an aqueous solution of perchloric acid, thus :—

$$\underset{\text{Perchloric acid.}}{2HClO_4} + \underset{\text{Iodine.}}{I_2} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Periodic acid.}}{2H_5IO_6} + \underset{\text{Chlorine.}}{Cl_2}.$$

On evaporation, periodic acid is obtained in deliquescent crystals, which melt at 133°, and are decomposed at 140° into iodic anhydride, oxygen, and water. The aqueous solution has a strong acid reaction and forms a series of salts, termed periodates, which as a rule have a somewhat complex composition, probably caused by the fact that iodic acid can act as a meta-acid, forming meta-salts, as potassium meta-periodate, KIO_4, and also forming para-salts in which the hydrogen of the two hydrating molecules of water fulfil acid functions, yielding a pentabasic acid. It is probable that iodine in this body acts as a pentavalent element, and that its graphic formula is



Barium para-periodate has the formula $Ba_5(IO_6)_2$: this salt may be heated to redness without decomposition.

262. Iodide of Nitrogen, NI_3.—On treating iodine in the cold with a concentrated solution of ammonia, a black powder is formed, which may be removed by filtration. On allowing the filter-paper to dry spontaneously, the resultant powder explodes most violently with the slightest touch, producing fumes of iodine. This powder probably consists of either the trioxide of nitrogen, or the compound NHI_2, the former being produced when the ammonia is in excess.

263. Fluorine.—Symbol, F. Atomic weight, 19·1.

Occurrence.—Fluorine occurs in nature in combination with calcium in fluor spar (calcium fluoride), CaF_2, and also in other minerals, among which is cryolite. The teeth of animals also contain traces of fluorine.

264. Preparation.—Fluorine is such an exceedingly active element that until recently all efforts to obtain it in the free state had proved unsuccessful. Whenever liberated by any

chemical reaction it immediately attacked the vessel in which it was contained, and so evaded all attempts at its isolation. Moissan has, however, succeeded in obtaining this element by the electrolysis of perfectly anhydrous hydrogen fluoride, HF. The apparatus employed consisted of a platinum U-tube fitted with delivery-tubes of the same metal and stoppers of fluor spar (calcium fluoride, CaF_2). The hydrogen fluoride was prepared by heating potassium hydrogen fluoride, KHF, and condensed in a receiver immersed in ice and salt. The anhydrous hydrogen fluoride was then introduced into the U-tube and cooled by immersion in liquid methyl chloride, boiling at $-23°$ C. A current from 20 large Bunsen cells was next passed through the liquid; traces of water were first driven off as hydrogen and ozone, at the same time the electric resistance of the liquid increased. In order to render it sufficiently conductive, a small quantity of dry potassium hydrogen fluoride was added, when hydrogen was evolved at the negative pole, and a colourless gas evolved at the positive pole, which was proved to be elementary fluorine. Under favourable conditions it was thus found possible to produce from 1·5–2 litres of fluorine in an hour.

265. **Properties.**—In this colourless gas, which is stated to have a very penetrating and disagreeable odour, crystallised silicon, adamantine boron, antimony, sulphur, phosphorus, and iodine take fire spontaneously and immediately. The gas decomposes water, with formation of ozone and hydrogen fluoride: it attacks metals much less readily, owing, most likely, to the formation of a superficial layer of fluoride, by which the metal is protected. Powdered iron burns in the gas when gently heated, with the production of sparks. On mixing the gas with hydrogen, combination immediately occurs, even in the dark, with explosion. Gold and platinum are attacked by the gas at 300–400°. It at once attacks perfectly dry glass, and also decomposes sodium chloride, with the liberation of chlorine. Fluorine combines directly with all the elements except oxygen, nitrogen, and carbon: no compound of fluorine with oxygen has been formed under any circumstances, but, by

indirect methods, fluoride of carbon may be produced. Such, in brief, are the properties in the free state of this the most active of all the chemical elements.

Hydrofluoric Acid.—Formula, HF. Molecular weight, 20·1. Density of vapour, 10·05. Boiling-point, 19·4°C. Specific gravity of liquid, 0·9879.

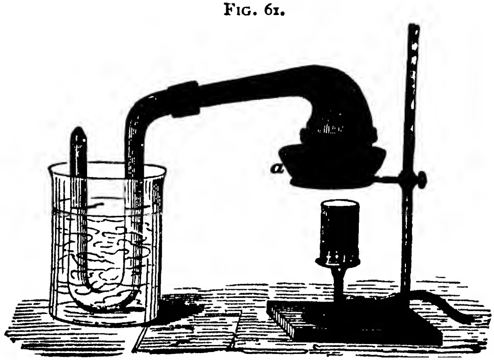
266. Preparation.—The preparation of hydrofluoric acid (hydrogen fluoride) in the absolutely anhydrous state is an exceedingly difficult operation. The best method of procedure is to heat dry hydrogen potassium fluoride in a platinum flask, passing the vapour which is evolved through a condenser consisting of a platinum tube surrounded by a freezing mixture, and collecting the condensed liquid in a platinum receiver also immersed in a mixture of ice and salt.

When not required absolutely dry, the acid in a concentrated form may be prepared by the action of the strongest sulphuric acid on finely powdered fluor-spar, CaF_2. On their being mixed, no gas is evolved until heat is applied, when the following change occurs—

$$\underset{\text{Calcium fluoride.}}{CaF_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Calcium sulphate.}}{CaSO_4} + \underset{\text{Hydrofluoric acid.}}{2HF.}$$

Dense white fumes are evolved, which condense on

FIG. 61.



being passed into a freezing mixture. For the preparation of the acid, the following apparatus may be employed. Fig. 61, *c*, is

a leaden retort having a joint round the middle, through which it is charged with the requisite mixture of sulphuric acid and fluoride. The retort stands on a sand-bath and is heated by the burner underneath. The stem of the retort is attached to a U-tube, also of lead, which stands in a freezing mixture, and in which the acid is condensed.

267. **Properties.**—Hydrofluoric acid, as prepared by the action of sulphuric acid on fluor spar, is a colourless, volatile, fuming liquid, containing water in small quantity. It is an intensely powerful caustic, and combines with water with great readiness, evolving much heat in so doing. The anhydrous acid has a density of 0·9879, but its mixture with water is accompanied with a sufficient diminution in volume to produce a liquid having the density 1·250. It dissolves the more easily attacked metals, with the formation of fluorides and the evolution of hydrogen gas; platinum and lead are unattacked by it.

The most striking property of hydrofluoric acid is its power of attacking glass and all other substances containing silicon, an action which only proceeds in the presence of moisture. If a piece of glass be coated with a thin layer of wax, it may have any design marked on it with the point of a needle, which scratches through the wax and lays bare the surface of the glass. On exposing glass which has been thus treated to the action of either dilute hydrofluoric acid or the fumes arising from powdered fluor spar and sulphuric acid, the glass is deeply etched where the wax has been removed. In this way a permanent marking on glass may be effected. Measuring-tubes and other pieces of chemical apparatus are often graduated and marked in this way.

Hydrofluoric acid is a monobasic acid, but forms very readily a series of double fluorides, of which potassium hydrogen fluoride may be taken as an example; it has the composition KHF_2 or KF,HF, and may be viewed as a compound of the molecules of hydrofluoric acid and potassium fluoride. This salt on being heated is decomposed into the normal fluoride and hydrofluoric acid, hence it is conveniently employed as a

source of the acid in its anhydrous form. The fluorides are all decomposed by sulphuric acid with evolution of hydrofluoric acid. Chlorine also decomposes them at a high temperature, with formation of chlorides. A mixture of hydrofluoric acid and nitric acid has no action on gold.

268. Review of the Halogens.—It will be seen that the members of this group of elements are characterised by possessing a remarkable similarity to each other. The connection between chlorine, bromine, and iodine is much closer than that with fluorine. Of these first three elements chlorine is a gas, bromine a liquid, and iodine a solid at ordinary temperatures. The density of the series increases with chlorine as the lowest and iodine as the highest. In the case of the binary compounds, the chemical activity diminishes with the increase in density; bromine being displaced from the bromides by chlorine, and iodine being displaced from iodides by either bromine or chlorine. The salts of silver and mercury are exceptions to this rule, as the chlorides and bromides may be converted into iodides by the action of concentrated hydriodic acid. In the case of the oxy-compounds, their relative stability is in the inverse order to that of the binary salts; the oxides of chlorine are so unstable as to explode on very slight elevations of temperature, while iodic anhydride is only decomposed at a temperature of 371°. Neither iodic acid and iodates nor bromic acid and bromates are decomposed by free chlorine; while periodic acid is formed by the displacement by iodine of the chlorine of perchloric acid. The compounds of these three elements are very similar in character; when in combination with the same element they form bodies having analogous formulæ and crystallising in the same form.

CHAPTER XIX

BORON AND SILICON

Boron.—Symbol, B. Atomic weight, 11·0. Specific gravity, crystallised form, 2·63.

269. **Occurrence.**—Boron does not occur plentifully in nature, the principal localities in which it is found being in certain volcanic districts of Tuscany and in California. It is not found in the free state, but in combination with oxygen.

270. **Preparation.**—Boron may be obtained from its oxide, B_2O_3, by heating it with potassium or sodium. The boron trioxide is coarsely powdered, mixed with the potassium cut in small pieces, and the mixture placed in an iron crucible already heated to redness. It is covered over with a layer of common salt, and stirred with an iron rod until the reaction is over. The still fluid mass is next poured into water acidulated with hydrochloric acid, which dissolves all except the boron, which remains as an amorphous brown or olive-green powder, which must be collected on a filter and well dried. The reaction which occurs is the following:—

$$\underset{\text{Boron trioxide.}}{B_2O_3} + \underset{\text{Sodium.}}{6Na} = \underset{\text{Sodium oxide.}}{3Na_2O} + \underset{\text{Boron.}}{2B.}$$

Amorphous boron obtained in this manner may be converted into a crystalline variety by fusion with aluminium. For this purpose a paste of amorphous boron and water is employed as a lining inside a crucible. In the centre a small ingot of aluminium, weighing some 8 or 10 grams is placed. The cover is luted down, and the whole crucible enclosed in a larger one, the space between being filled with charcoal, and the outer cover luted in place. The crucibles are then exposed to a white heat for some two hours, and allowed to cool. The melting aluminium dissolves the boron, from which, on cooling, it crystallises out in yellowish octahedral crystals. The aluminium may be dissolved by either caustic soda or dilute hydrochloric acid, when the boron crystals remain. These

crystals are not absolutely pure, but contain 2 to 4 per cent of carbon.

271. Properties.—The amorphous form of boron is slightly soluble in water, and is not oxidised by either air or oxygen at ordinary temperatures. Below redness it takes fire and burns, with the formation of boron trioxide, B_2O_3, which forms a superficial coating and so protects the interior from further oxidation. It may also be oxidised by treatment with nitric acid and other oxidising agents.

The crystallised form is exceedingly hard, scratching the ruby and only being excelled by the diamond, which stone it sensibly abrades. It is infusible in the heat of the oxyhydrogen blowpipe, and in oxygen burns, with the formation of the trioxide on the surface, by which it is protected from further action. In chlorine it burns, with the formation of boron chloride, BCl_3. All acids are without action on boron. The element somewhat resembles carbon in properties, and is trivalent in most of its compounds.

Boron Trioxide (Boric Anhydride).—Formula, B_2O_3. Molecular weight, 69·78.

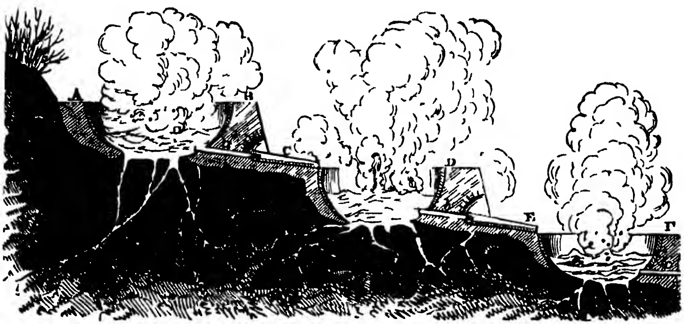
Boric Acid.—Formula, H_3BO_3. Molecular weight, 61·78.

272. Occurrence.—Only one oxide of boron is known; this, in combination with water as boric acid, occurs in Tuscany, and the sodium salts are found in Thibet and California.

273. Extraction.—The Tuscan boric acid is brought to the surface by jets of steam termed *suffioni*, which escape from regions subject to subterranean volcanic heat; the springs so formed contain boric acid in small quantity. To concentrate the dilute solution thus occurring, a series of basins are constructed of rough masonry around the suffioni themselves (fig. 62). A B is one of such basins, into which the water is conducted. The heat of the gases escaping from the suffioni concentrates the liquid by evaporation; after some twenty-four hours it is allowed to flow into a similar basin built at a lower level, and thus undergoes successive concentrations in a series

of vessels until sufficiently strong. The liquid is then allowed to cool and boric acid crystallises out in the crude form.

FIG 62.



274. **Properties.**—Boric acid occurs in scaly crystals having a somewhat pearly lustre, and the same greasy feeling to the touch as is possessed by graphite. The acid is soluble in cold water to the extent of about 4 per cent.; boiling water dissolves about one-third of its own weight of boric acid. In solution this acid has only a very faintly sour taste; it changes litmus to the port-wine tint also produced by carbonic acid. The carbonates are decomposed by boric acid, particularly with a hot solution, but in the cold, excess of carbon dioxide displaces a portion of boric acid from its salts. Boric acid stains turmeric paper a brown colour, which colour is unaltered by treatment with hydrochloric acid: the alkalies produce a stain of the same colour, but in this case, the yellow tint is restored by the action of a free acid.

Boric acid imparts a vivid green tint to a bunsen flame, and also to burning alcohol. On being heated the acid is first decomposed into water and metaboric acid:—

$$\underset{\text{acid.}}{H_3BO_3} = \underset{\text{Metaboric acid.}}{HBO_2} + \underset{\text{Water.}}{H_2O.}$$

With still further heat, the meta-acid is decomposed, leaving behind a transparent glassy substance, which consists of boron trioxide:—

$$\underset{\text{Metaboric acid.}}{2HBO_2} = \underset{\text{Boron trioxide.}}{B_2O_3} + \underset{\text{Water,}}{H_2O.}$$

Although boric acid has at ordinary temperatures but feebly acid properties, yet at a sufficiently intense heat it displaces almost all other acids from their combinations with bases; a fact due to the very slight volatility of boric anhydride at high temperatures.

In addition to these two forms of boric acid, salts are also known which correspond to another form, termed pyro-boric acid, $H_2B_4O_7$. Thus borax, the best known salt of boric acid, has the formula, $Na_2B_4O_7$, which may also be written $(NaBO_2)_2$, B_2O_3; that is, two molecules of the meta-borate combined with a molecule of the trioxide. Owing to this tendency of the borates to unite with additional molecules of the anhydride, the greater number of them are somewhat complex in composition. Borax is prepared in large quantity by addition of sodium carbonate to the hot solution of boric acid; the liquid on cooling deposits this salt in large colourless crystals. Although borax contains an excess of boric acid, it is feebly alkaline in reaction to litmus. Borax in a fused state possesses in a remarkable degree the property of dissolving metallic oxides, thus forming borates which frequently have characteristic colours.

275. Industrial Applications.—Boric acid is a powerful antiseptic, and is somewhat largely used as a milk and fish preservative. Very small quantities are sufficient for this purpose, and being practically tasteless, its use does not confer any objectionable flavour: so far as is known, boric acid is without any injurious action on the human system.

Borax is largely used as a flux by the silver and gold refiner, and also by the tin- and copper-smith in order to obtain oxide-free metallic surfaces for soldering and brazing purposes.

276. Other Boron Compounds.—Boron combines with hydrogen, and also the halogens, forming a series of compounds represented by the following formulæ: BH_3, BCl_3, BBr_3, and BF_3.

Hydrofluoboric Acid, HBF_4, or HF,BF_3.—When gaseous boron fluoride is brought into contact with water, boric and hydrofluoboric acids are formed, according to the equation

$$\underset{\text{Boron fluoride.}}{8BF_3} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Hydrofluoboric acid.}}{6HBF_4} + \underset{\text{Boric acid.}}{2H_3BO_3}$$

This acid forms a series of salts known as fluoborates, or borofluorides, of which KBF_4, potassium fluoborate, is an example. This acid may be viewed as a compound of one molecule each of hydrofluoric acid and boron fluoride. The more frequent name applied to the salts is that of borofluoride; it has, however, the objection that the termination *ide* is used for other than a binary compound.

Boron Nitride, BN.—This is one of the few instances of a compound being formed by the direct union of nitrogen with another element: for on passing nitrogen over boron at a white heat, this body is produced. It is a colourless, light, amorphous powder, of no special importance.

Silicon.—Symbol, Si. Atomic weight, 28·0. Specific gravity of crystals, 2·49.

277. **Occurrence.**—Silicon does not occur free in nature, but, next to oxygen, is the most plentiful of all the elements. Its oxide, SiO_2, occurs in the free state, as flint and quartz, and also in combination, as one of the principal constituents of most rock formations except those of coal and limestone.

278. **Preparation.**—Silicon forms a potassium compound, having the formula $(KF)_2SiF_4$, termed potassium silicofluoride, and very similar in properties to potassium borofluoride, already described. On heating a mixture of potassium and this silicofluoride, the following reaction occurs :—

$$\underset{\text{Potassium silicofluoride.}}{(KF)_2SiF_4} + \underset{\text{Potassium.}}{4K} = \underset{\text{Silicon.}}{Si} + \underset{\text{Hydrofluoric acid.}}{6KF.}$$

In order to effect this reaction, about equal weights of the two bodies are heated strongly in an iron tube, until all reaction is over. When perfectly cold the mixture is treated with water, when hydrogen is evolved by the excess of potassium remaining. There remains an insoluble body, which is carefully washed until no trace of alkali remains; this, on being filtered and dried, leaves a brown powder, which consists of amorphous silicon.

Intense ignition of this silicon results in a diminution of

volume, and a denser form of silicon, much less chemically active. This substance is apparently identical with that formed by igniting together potassium silicofluoride and aluminium, when the following reaction occurs.

$$\underset{\substack{\text{Potassium}\\ \text{silicofluoride.}}}{3(KF)_2SiF_4} + \underset{\text{Aluminium.}}{4Al} = \underset{\substack{\text{Hydrofluoric}\\ \text{acid.}}}{6HF} + \underset{\substack{\text{Aluminic}\\ \text{fluoride.}}}{2Al_2F_6} + \underset{\text{Silicon.}}{3Si.}$$

The fused mass thus produced is allowed to cool, and treated first with hydrochloric and then with hydrofluoric acid; the silicon remains behind as black, hexagonal, shining crystals which, from their resemblance to graphite, have been termed graphitoidal silicon.

Silicon may also be obtained in the form of octahedral crystals by heating together potassium silicofluoride, sodium, and pure zinc. The residual mass is exhausted, first by hydrochloric acid, and afterwards by nitric acid. These crystals are sufficiently hard to cut glass.

279. Properties.— In the amorphous form, silicon is insoluble in water, and a non-conductor of electricity. It is inflammable in either air or oxygen, forming as it burns a layer of silica, SiO_2, with which the fragments are coated, and which by shutting off the air prevents the interior from being oxidised. Hydrofluoric acid, or a solution of potassium hydrate, dissolves silicon, which is, however, unacted on by either nitric or sulphuric acids. The ignited form of amorphous silicon is much more difficult to burn; even ignition in the oxy-hydrogen blowpipe flame does not cause it to take fire.[1] Pure hydrofluoric acid is without action on it, but it is rapidly attacked by a mixture of nitric and hydrofluoric acids. The graphitoidal variety of silicon is a conductor of electricity, and possesses the same general reactions as the ignited form, with which possibly it is identical.

The octahedral form is very hard, and is also unattacked by hydrofluoric acid, or any mixture of acids, except that of nitric and hydrofluoric acids.

It will be seen that considerable resemblance exists between silicon and carbon; both possess two crystalline varieties

[1] The word ignition is used by the chemist to signify subjection to intense heat, independently of whether or not the substance burns.

which respectively somewhat resemble each other in character. They both yield an amorphous form. In this they are also resembled by boron, which likewise yields a very hard crystalline variety. In their chemical relationships carbon and silicon are also found to be very similar to each other. This will be more evident on examining the principal silicon compounds, which in composition are identical with carbon compounds with the same elements.

Silicon Dioxide, Silica.—Formula, SiO_2. Molecular weight, 59·92. Specific gravity as quartz, 2·6.

Silicic Acid.—Formula, H_4SiO_4.

280. Occurrence.—As has already been mentioned, silica is widely distributed in nature as a rock constituent. Quartz and amethyst are examples of a crystalline variety, and agate, chalcedony, opal, and flint consist of silica in an amorphous form mixed with more or less of the crystalline variety.

281. Preparation.—Silica is sometimes termed silicic anhydride because with water it forms acids, and unites with bases to produce salts. Prolonged boiling with concentrated solutions of caustic potash or soda dissolves crystalline silica very slowly, but has a more rapid action on the amorphous varieties. When fused with either of the alkaline carbonates an alkaline silicate is formed :—

$$\underset{\text{Silica.}}{SiO_2} + \underset{\text{Potassium carbonate.}}{2K_2CO_3} = \underset{\text{Potassium silicate.}}{K_4SiO_4} + \underset{\text{Carbon dioxide.}}{2CO_2}.$$

Carbon dioxide escapes, and the remaining silicate is soluble in water, and constitutes the substance known as water-glass. If hydrochloric acid be added to the solution, potassium chloride and silicic acid are formed :—

$$\underset{\text{Potassium silicate.}}{K_4SiO_4} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Potassium chloride.}}{4KCl} + \underset{\text{Potassium silicate.}}{H_4SiO_4}.$$

If the solution be concentrated the silicic acid separates out as a gelatinous mass, but if sufficiently dilute it remains dissolved. On the solution being placed in a drum with the bottom made of parchment paper, and this floated in its turn in a vessel of water, the potassium chloride, being a crystalline

body, diffuses through the membrane, and a pure solution of silicic acid remains behind. In this way a solution of quartz or silica is produced. This solution may be concentrated by careful evaporation until it contains about 14 per cent. of silica; but the solution of this degree of strength is liable to assume the gelatinous form. On further concentration the silica separates out, and on evaporation to complete dryness remains as an amorphous white powder, insoluble in water and acids.

282. Properties.—Quartz is, when pure, transparent and colourless; it is so hard that it scratches glass. Quartz crystals consist of hexagonal prisms capped with hexagonal pyramids. Quartz is insoluble in water and all acids, except hydrofluoric acid, by which it is readily attacked. It is not liquefied by the heat of the strongest furnaces, but may be melted into a glassy mass by the oxy-hydrogen blowpipe.

Silicic acid, as obtained by the process of dialysis above described, is colourless and tasteless; it is a very weak acid, and may be displaced from its union with bases by even such a feeble acid as carbonic acid. This fact is strikingly exemplified by the slow 'weathering' of granitic rocks by the action of the carbonic acid from the atmosphere by which they are attacked. The alkaline silicates are slowly dissolved as carbonates, and are washed away, leaving behind the more insoluble rocky constituents. On the other hand, at a high temperature, owing to its non-volatility, silica is able to displace almost every acid from its compounds with bases. The decomposition of the alkaline carbonates by silica is an illustration of this property.

Silicic acid has been represented as a tetrabasic acid with the formula, H_4SiO_4, but it is found impossible to prepare with certainty any definite hydrates of silica; therefore all formulæ given to the acids are really derived from those showing the constitution of its salts. The silicates constitute a most important natural group of substances, as almost all rock-forming minerals belong to this class. The following are examples of a few typical silicates, with the corresponding acids of which they may be supposed to be salts.

ACIDS.	SALTS.	
Metasilicic acid, H_2SiO_3 or SiO_2,H_2O.	Potassium Metasilicate,	K_2SiO_3.
	Wollastonite,	$CaSiO_3$.
	Augite,	$CaMgSiO_3$.
Orthosilicic acid, H_4SiO_4 or $SiO_2(H_2O)_2$.	Olivine,	Mg_2SiO_4.
	Forge cinder,	Fe_2SiO_4.
	Garnet,	$Al_2Ca_3(SiO_4)_3$.
H_4SiO_4,H_2SiO_3.	Meerschaum,	Mg_2SiO_4,H_2SiO_3.
$H_6Si_2O_7$.	Serpentine,	$Mg_3Si_2O_7$.
$H_4Si_3O_8$ or $(SiO_2)_3,(H_2O)_2$.	Orthoclase felspar,	$Al_2K_2(Si_3O_8)_2$.

It is difficult to satisfactorily trace out the constitution of the more complex silicates, particularly as it is impossible to determine their true molecular formulæ; those given are in most cases the simplest possible formulæ that can be derived from the percentage composition. It is frequently more satisfactory to represent these bodies by formulæ showing the number of molecules of anhydride and base of which they are composed. For example, felspar thus becomes $(SiO_2)_6$ AlO_3K_2O, and meerschaum $(SiO_2)_2(MgO)_2,H_2O$.

The alkaline silicates are soluble in water and constitute the substance known as water-glass. Certain natural hydrated silicates, called zeolites, are insoluble in water, but are dissolved by hydrochloric acid, with the formation of gelatinous silicic acid. Other silicates are insoluble in water and all acids except hydrofluoric acid. Clays are natural silicates of alumina, kaolin or so-called china clay, being formed by the decomposition of felspar by atmospheric carbonic acid.

283. Industrial Applications.—The various clays are used in the making of bricks and earthenware, the purest clays being marked by extreme infusibility. Glass is also a mixture of silicates. The soluble alkaline silicates possess detergent properties, and are employed in the manufacture of soap.

284. Silicon Hydride, SiH_4.—Silicon hydride is a gaseous body, having a density of 16. It may be prepared by the action of dilute hydrochloric acid on magnesium silicide, $SiMg_2$.

To obtain this body 8 parts of anhydrous magnesium chloride, 7 parts of sodium fluoride, 2 parts of sodium chloride, and 4 parts of finely divided sodium are placed in a red-hot crucible which is immediately closed. On cooling, a mass of substance remains which contains magnesium silicide together with excess of magnesium. On placing this substance in a gas delivery-flask, fitted with wide exit-tube, the evolution of gas may be caused by first *filling* the flask with air-free water, and then adding carefully dilute hydrochloric acid, when the following reaction occurs :—

$$\underset{\text{Magnesium silicide.}}{SiMg_2} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Magnesium chloride.}}{2MgCl_2} + \underset{\text{Silicon hydride.}}{SiH_4}.$$

The end of the delivery-tube of the apparatus should be placed under water in a pneumatic trough ; as each bubble of gas arrives at the surface it takes fire spontaneously, forming a vortex ring of smoke which consists of finely divided silica. In this experiment the excess of magnesium causes the evolved gas to be associated with free hydrogen ; if steps be taken to obtain the gas in a state of absolute purity, it is no longer spontaneously inflammable, but still takes fire with a slight elevation of temperature. If a jar of the gas be collected and inflamed, the hydrogen burns and deposits a film of amorphous silicon around the neck of the jar.

285. Silicon Chloride, $SiCl_4$.—This body is a volatile liquid boiling at 58° C. It may be prepared by heating together a mixture of silica and charcoal in chlorine gas, when the following change occurs—

$$\underset{\text{Silica.}}{SiO_2} + \underset{\text{Carbon.}}{2C} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Silicon chloride.}}{SiCl_4} + \underset{\text{Carbon monoxide.}}{2CO}.$$

The silicon and chlorine combine, and simultaneously the oxide of carbon is formed.

Silicon bromide and iodide, $SiBr_4$, and SiI_4, are formed by similar reactions and have corresponding formulæ.

286. Silicon Fluoride, SiF_4.—This body is a gas possessing a suffocating odour, and is formed wherever hydrofluoric acid

acts upon silica, or a silicate, in the presence of a powerful drying agent. It may conveniently be prepared by gently heating a mixture of fluor-spar with an excess of fine sand (silica) and sulphuric acid. Hydrofluoric acid is first evolved, and then attacks the silica—

$$\underset{\text{Silica.}}{SiO_2} + \underset{\text{Calcium fluoride.}}{2CaF_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Silicon fluoride.}}{SiF_4} + \underset{\text{Calcium sulphate.}}{2CaSO_4} + \underset{\text{Water.}}{2H_2O.}$$

It is this reaction by which hydrofluoric acid acts on glass and all silicates. Silicon fluoride is immediately decomposed on coming in contact with water.

The similarity in constitution between silicon and carbon compounds is strikingly shown in the bodies just described; the analogous carbon compounds are below placed side by side with them for comparison :—

Silicon	hydride,	SiH_4.	Carbon	hydride,	CH_4.
,,	chloride,	$SiCl_4$.	,,	chloride,	CCl_4.
,,	bromide,	$SiBr_4$.	,,	bromide,	CBr_4.
,,	iodide,	SiI_4.	,,	iodide,	CI_4.
,,	fluoride,	SiF_4.	,,	fluoride,	CF_4.
,,	chloroform,	$SiHCl_3$.	,,	chloroform,	$CHCl_3$.
,,	oxide,	SiO_2,	,,	oxide,	CO_2.

This list is capable of much further extension.

237. Hydrofluosilicic Acid, H_2SiF_6.—When silicon fluoride is decomposed by the action of water the following reaction occurs :—

$$\underset{\text{Silicon fluoride.}}{3SiF_4} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Silicic acid.}}{H_4SiO_4} + \underset{\text{Hydrofluosilicic acid.}}{2H_2SiF_6.}$$

In the first place, gelatinous silicic acid and hydrofluoric acid are formed; the hydrofluoric acid unites with silicon fluoride and produces hydrofluosilicic acid, which may be regarded as $(HF)_2SiF_4$. In thus preparing this acid there is considerable risk of altogether stopping the end of the delivery-tube with the silicic acid; this is avoided by placing a little mercury in the vessel containing the water, and keeping the end of the delivery-tube well below the surface of the metal.

The silicic acid is removed by filtration, and the hydrofluosilicic acid concentrated by evaporation at ordinary temperatures *in vacuo*, when there remains a colourless, strongly acid liquid. Hydrofluosilic acid does not attack glass, but if evaporated in a vessel of that material it decomposes with the escape of silicon fluoride, and the hydrofluoric acid remaining corrodes the glass on the surface. Hydrofluosilicic acid forms salts known as silicofluorides, but better termed fluosilicates, for the same reason as that which holds with the fluoborates, which show some similarity in constitution. The fluosilicates of barium ($BaSiF_6$), calcium, potassium (K_2SiF_6), and sodium are insoluble in water; most others are soluble.

CHAPTER XX

PHOSPHORUS

Phosphorus.—Symbol, P. Atomic weight, 30 96. Density, 61·92. Specific gravity of ordinary variety, 1·83. Molecular weight, 123·84.

288. Occurrence.—Phosphorus is not found free in nature, but occurs in many igneous rocks; thus minute crystals of minerals containing phosphorus may be discerned by the microscope in granite. These rocks, by their decomposition, produce soil which also contains phosphorus, as phosphates. These are assimilated by plants and are found especially in the seeds; thus considerable quantities of phosphorus occur in wheat. In their turn animals assimilate the phosphates of vegetable food, and use them in building up certain compounds occurring in the brain and elsewhere, but more especially in the formation of bone, the mineral part of which, or bone-ash, consists largely of calcium phosphate. The fossil substance known as 'coprolites' is also principally composed of calcium phosphate. From this compound the phosphorus of commerce is prepared.

289. Manufacture.—The first step in the preparation of

phosphorus is to mix bone-ash with two-thirds of its weight of sulphuric acid diluted with water. Calcium phosphate is insoluble, but under this treatment is transformed into a soluble acid phosphate, commonly known as superphosphate of lime. The following equation represents the change which occurs :—

$$\underset{\substack{\text{Calcium}\\\text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Calcium}\\\text{hydric phosphate.}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{2CaSO_4.}$$

The calcium sulphate is allowed to settle, and then the clear solution of acid phosphate is evaporated down to the consistency of a syrup and mixed into a paste with powdered charcoal. This is dried and then heated to low redness in an earthenware retort, the stem of which dips under water.

The first result of the application of heat is that the acid or hydric phosphate loses its water, being converted into a salt known as the metaphosphate :—

$$\underset{\substack{\text{Calcium}\\\text{hydric phosphate.}}}{CaH_4(PO_4)_2} = \underset{\substack{\text{Calcium}\\\text{metaphosphate.}}}{Ca(PO_3)_2} + \underset{\text{Water.}}{2H_2O.}$$

$Ca H_4 P_2 O_8 = Ca P_2 O_6 + H_4 O_2 = 2H_2O.$

The metaphosphate is at the high temperature decomposed by the charcoal ; thus :—

$$\underset{\substack{\text{Calcium}\\\text{metaphosphate.}}}{3Ca(PO_3)_2} + \underset{\text{Carbon.}}{10C} = \underset{\text{Phosphorus.}}{P_4} + \underset{\substack{\text{Calcium}\\\text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{10CO.}$$

The phosphorus thus produced distils over, and is purified by re-distillation and squeezing through wash-leather under warm water.

290. Properties.—Phosphorus is an almost colourless (slightly yellow) and transparent solid, having at ordinary temperature the consistency of bees'-wax, and may be cut with a knife. At the freezing-point it becomes considerably harder and more brittle ; it then shows, on being broken, evidences of crystalline structure. Phosphorus melts at a temperature of 44·3° and boils at 290° C.; the vapour is colourless. The density of phosphorus vapour is 61·92, or double the atomic weight. The molecular weight is 123·84, and therefore phosphorus, like sulphur, contains more than two atoms in the

molecule. While the sulphur molecule is hexatomic, that of phosphorus is tetratomic. At high temperatures the density of phosphorus vapour diminishes, and the element exists in part, at least, as diatomic molecules. When exposed to the air phosphorus is seen to evolve small quantities of smoke, and in the dark is distinctly luminous. From this property it has received its name, which signifies light-bearer. The fumes emitted consist of phosphorus trioxide, P_2O_3, and the light is due to slow combustion of the phosphorus. This element is characterised by its great inflammability; at a temperature of about 44°, a very little over its melting-point, it takes fire, and, as the student already knows, burns brightly, with the formation of phosphorus pentoxide. Phosphorus combines readily, not only with oxygen, but also the halogens, and with sulphur. Phosphorus is easily ignited by a slight amount of friction: the greatest possible care must therefore be exercised in handling and cutting the phosphorus. The last operation is, in fact, always more safely performed under water. Phosphorus is insoluble in water, slightly soluble in alcohol or ether, and readily soluble in carbon disulphide. A carbon disulphide solution of phosphorus deposits the phosphorus in well-defined crystals on its evaporation. If poured over paper, so as to form a thin layer, the finely divided phosphorus left on evaporation oxidises so rapidly as to take fire and also inflame the paper.

Mixtures of phosphorus with potassium chlorate or nitrate explode most violently on the slightest percussion. Owing to the readiness with which it undergoes oxidation, phosphorus is kept under water, which liquid it does not decompose.

291. Red or Amorphous Phosphorus.—In addition to the yellow variety, phosphorus occurs in another totally distinct form, known as red or amorphous phosphorus. If ordinary phosphorus be maintained at a temperature of 240° for some time, it is more or less completely changed into an opaque reddish mass, without any alteration of weight. This, on purification from the ordinary form, constitutes amorphous phosphorus.

On the large scale, amorphous phosphorus is manufactured

by heating the ordinary phosphorus for a period of some days in an iron vessel having only a small aperture. The temperature is carefully regulated to 240°, and when the change has proceeded as far as practicable the phosphorus is removed. In order to free it from traces of ordinary phosphorus, the resultant mass is treated with carbon disulphide, which dissolves the ordinary form, but is without action on the red variety. Or, the phosphorus may also be digested with caustic soda solution, until the whole of the yellow phosphorus present is displaced as phosphoretted hydrogen ; red phosphorus is unacted on by sodium hydrate. When thus prepared red phosphorus occurs as a dark red powder. This modification differs most remarkably from the yellow kind. It is not luminous when exposed to air, does not oxidise, and so need not be kept under water. It remains solid up to a temperature beyond 250°, and does not take fire when heated in the air until 260° is reached. At this point it becomes changed into the yellow variety, and burns. If the heating be conducted in a retort filled with carbon dioxide, so as to prevent combustion, the same weight of yellow phosphorus is produced, proving most clearly that the two varieties are only allotropic modifications of one and the same element. Further, both, on being burned, produce the same weight of phosphorus pentoxide.

The change from the yellow to the red form takes place much more readily and at lower temperatures in the presence of traces of iodine.

Ordinary phosphorus is violently poisonous, while the red form of the element is without any action on the human economy.

292. Industrial Applications.—The ready inflammability of phosphorus has caused it to be largely employed as a means of obtaining light. The earlier lucifer matches introduced during the present century consisted of slips of wood, dipped in sulphur and tipped with a phosphorus composition. They were briskly drawn through a double fold of glass-paper, and thus ignited. At present the ordinary lucifer match is made by first dipping the prepared wooden slips in either sulphur or

melted paraffin, by which they are rendered inflammable. A tipping composition is prepared which consists of phosphorus mixed with some oxidising substances; of such mixtures, the following are examples :—

Phosphorus	4·7	Phosphorus	8·0
Gum	14·0	Glue	21·0
Water	12·0	Lead peroxide	24.0
Lead peroxide	65·0	Saltpetre	24·0

This is applied to the tips of the matches, and allowed to dry on. Very slight friction on any rough surface causes the match to take fire.

Of late years, red phosphorus has largely replaced the ordinary variety in match manufacture. It has the advantage of being non-poisonous, thus avoiding the risk of poison especially to young children who readily eat matches, in common with fragments of broken glass, and other similar articles of diet. Further, the substitution of red phosphorus is a most valuable boon to those engaged in the manufacture of matches, as the fumes of ordinary phosphorus vapour induce a most painful and serious bone-disease. The red phosphorus matches are introduced to the public under the name of 'safety' matches, because they can only with difficulty be caused to light otherwise than by friction on the prepared surface of the box. The matches in this case are tipped with a composition containing the oxidising substance of which the following is an example :—

Potassium chlorate	6
Antimonious sulphate	2–3
Glue	1

The phosphorus is applied to the side of the box in a mixture such as the following :—

Amorphous phosphorus	10
Manganese dioxide, or antimonious sulphide	8
Glue	3-6

Very slight friction between the match and the phosphorus surface causes ignition.

Hydrogen Phosphides.—Phosphoretted Hydrogen. Formula, PH_3. Molecular weight, 33·96. Density, 16·98. Specific gravity, 1·17.

293. **Preparation.**—On boiling a strong solution of caustic soda or potash with phosphorus, a spontaneously inflammable gas is evolved, having the odour of putrid fish, and approximately the composition PH_3. This gas is phosphoretted hydrogen or phosphine. The caustic soda and phosphorus should be introduced into a flask, together with water, and then the whole of the air *completely* displaced either by carbon dioxide or coal-gas. The delivery-tube must be well fitted, and its exit end should lead under the surface of water in a pneumatic trough. On applying heat to the flask, bubbles of gas arise, which gradually displace the coal-gas. Then as each bubble rises through the water and meets the air, it at once bursts into flame, forming a beautiful series of vortex rings of smoke, consisting of phosphorus pentoxide. Jars of the gas may be collected in the ordinary way in the trough over water; care must be taken, however, that they do not come in contact with air.

The reaction by which phosphoretted hydrogen is thus produced is a somewhat complicated one, and may be thus expressed :—

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Potassium hydrate.}}{3KHO} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Potassium hypophosphite.}}{3KH_2PO_2} + \underset{\text{Phosphoretted hydrogen.}}{PH_3}.$$

In addition to the phosphoretted hydrogen, PH_3, traces of another phosphide of hydrogen, P_2H_4, are formed. It is the presence of these which causes the gas to inflame spontaneously. The gas on standing loses this property, because the second phosphide, P_2H_4, suffers decomposition.

In the above method of preparing the gas, milk of lime (*i.e.* lime suspended in water) may be employed instead of caustic potash.

This second phosphide may be obtained by passing the phosphoretted hydrogen through a U-tube surrounded by a mixture of ice and salt. It is a volatile, colourless liquid, taking

fire immediately on coming in contact with air. This liquid phosphoretted hydrogen has the formula P_2H_4, and the presence of traces of its vapour in hydrogen, carbon monoxide, or other inflammable gas, as well as gaseous phosphoretted hydrogen, causes them to take fire spontaneously when coming in contact with air. Liquid phosphoretted hydrogen is also produced when calcium phosphide, CaP, is treated with water :—

$$\underset{\text{Calcium phosphide.}}{2CaP} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Calcium hydrate.}}{2Ca(HO)_2} + \underset{\text{Phosphoretted hydrogen.}}{P_2H_4}.$$

This liquid phosphide is readily decomposed by light, or the action of hydrochloric acid, into a solid phosphide, P_4H_2, and gaseous phosphoretted hydrogen :—

$$\underset{\text{Liquid phosphoretted hydrogen.}}{5P_2H_4} = \underset{\text{Solid phosphoretted hydrogen.}}{P_4H_2} + \underset{\text{Gaseous phosphoretted hydrogen.}}{6PH_3}.$$

294. Properties.—Gaseous phosphoretted hydrogen is a colourless gas, having a most unpleasant odour of putrid fish. It is readily inflammable, burning with the production of phosphorus pentoxide and water. The compounds of phosphorus somewhat resemble in their constitution and properties those of nitrogen. It will be seen that this hydride is similar in constitution to ammonia, NH_3. It has, however, no action on litmus paper, but nevertheless shows in some cases slightly basic properties: for example, it combines with hydriodic acid :—

$$\underset{\text{Hydrogen phosphide.}}{PH_3} + \underset{\text{Hydriodic acid.}}{HI} = \underset{\text{Phosphonium iodide.}}{PH_4I}.$$

The body thus produced, phosphonium iodide, PH_4I, is analogous in composition to ammonium iodide, NH_4I.

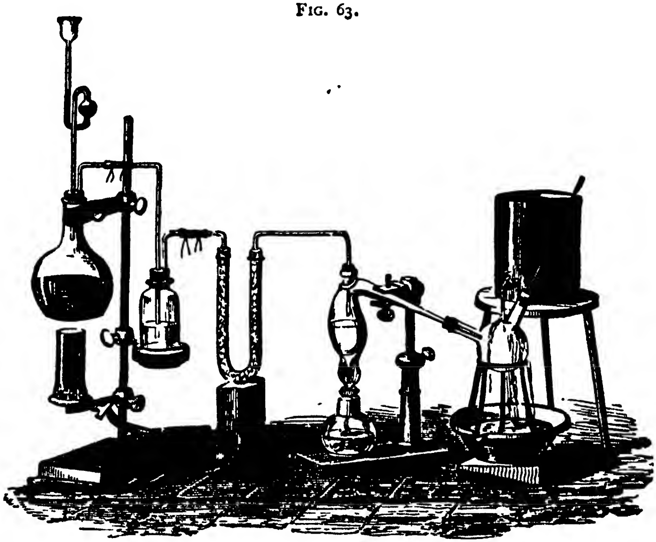
As already stated, by the ordinary methods of preparing PH_3, it is accompanied by traces of the liquid phosphide, P_2H_4. If a jar of the gas be left standing for some time, the inside will be found covered with a film of yellow solid matter. This is produced by the condensation and subsequent decomposition of the liquid phosphide, with the production of the solid

phosphide, P_4H_2. This body is a yellow powder which takes fire at about a temperature of 150° C.

Phosphorous Chloride.—Formula, PCl_3. Molecular weight, 137·07. Density, 68·53. Specific gravity of liquid, 1·6129 at 0°C. Boiling-point, 76°.

295. **Preparation.**—This body may be prepared by passing dry chlorine over excess of dry phosphorus contained in a retort, the amorphous variety being preferably employed. The following arrangement of apparatus (fig. 63), is con-

FIG. 63.



venient. On the left-hand side is shown the chlorine flask, wash-bottle, and drying-tube. The retort is gently heated by a spirit-lamp, and has its stem introduced into a receiver kept cold by a current of water flowing over its outside. Phosphorous chloride collects in the receiver.

296. **Properties.**—The trichloride of phosphorus is a colourless, fuming, volatile liquid, which readily dissolves phosphorus. Water decomposes it, with the formation of hydrochloric and phosphorous acids ;—

PCl_3	+	$3H_2O$	=	H_2PHO_3	+	$3HCl$.
Phosphorous chloride.		Water.		Phosphorous acid.		Hydrochloric acid.

Phosphoric Chloride.—Formula, PCl_5. Molecular weight, 207·81.

297. Preparation.—This compound is formed when phosphorus is treated with excess of chlorine; it may be produced by leading dry chlorine into a flask containing phosphorus trichloride and placed underneath a stream of cold water. The chlorine is absorbed and the trichloride becomes converted into a white or yellowish-white mass of pentachloride. It is also prepared by passing chlorine in excess through a solution of phosphorus in carbon disulphide.

298. Properties.—This body is a white crystalline powder which, under ordinary atmospheric pressures, sublimes without fusion. The vapour is at first colourless, but darkens with increase of temperature, and at the same time diminishes in density. This is due to its dissociation into the trichloride and free chlorine. Under pressure, the solid may be melted into a liquid which on further increase of temperature boils. It is very deliquescent, and in the presence of water is decomposed into phosphoric and hydrochloric acids.

PCl_5	+	$4H_2O$	=	$5HCl$	+	H_3PO_4.
Phosphoric chloride.		Water.		Hydrochloric acid.		Phosphoric acid.

299. Phosphorus Pentafluoride, PF_5.—By treating arsenic trifluoride with phosphorus pentachloride a compound is formed having the composition PF_5. This body, which is a colourless gas, has a density of 63; and is stable at very high temperatures, showing no signs of dissociation. The existence of this compound furnishes valuable evidence of the pentavalent nature of phosphorus in a stable gaseous molecule.

300. Phosphorus Oxides and Acids.—Phosphorus and oxygen combine to produce four oxides:—

Phosphorus monoxide, P_4O.

Phosphorus trioxide (phosphorous anhydride), P_2O_3 (P_4O_6).

Phosphorus tetroxide, P_2O_4.
Phosphorus pentoxide, (phosphoric anhydride), P_2O_5.

Four oxy-acids of phosphorus are also known :—

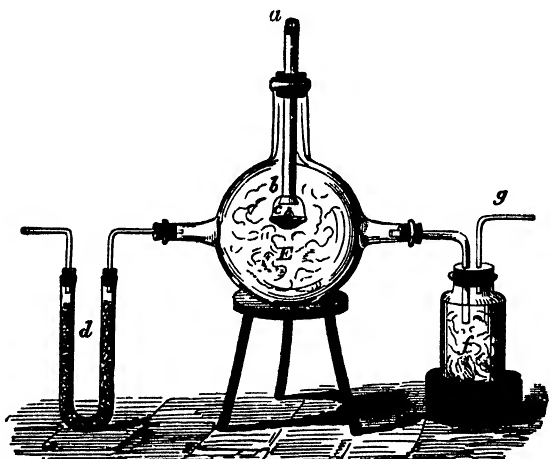
Hypophosphorous acid, HPH_2O_2.
Phosphorous acid, H_2PHO_3.
Hypophosphoric acid, H_2PO_3.
Phosphoric acid, H_3PO_4.

Phosphoric acid, being the most important of these bodies, will, in conjunction with its anhydride, be considered first.

Phosphorus Pentoxide.—Formula, P_2O_5. Molecular weight, 141·72.

301. Preparation.—Phosphorus pentoxide is readily prepared by burning phosphorus in excess of air or oxygen.

FIG. 64.



To produce this body in large quantity the above apparatus is employed (fig. 64). Air is drawn through the apparatus by means of an aspirator attached to *g*, and is thoroughly dried by passing through the U-tube *d*, filled with pumice moistened with sulphuric acid. Phosphorus is burned in the spoon *c*, suspended in the middle of the globe E; the anhydride partly collects in E, and part passes over into *f*, which bottle may be used

as a storage for the whole of the anhydride prepared. It is necessary to keep this bottle well stoppered if the anhydride is to be preserved in the pure state.

302. **Properties.**—Phosphoric anhydride is a white flocculent powder which possesses great attraction for water, producing a hissing noise when dropped into that liquid and evolving great heat. It in this way forms phosphoric acid :—

$$\underset{\text{Phosphoric anhydride.}}{P_2O_5} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphoric acid.}}{2H_3PO_4}.$$

Phosphoric Acid.—Formula, H_3PO_4. Molecular weight, 97·80.

303.—**Preparation.**—This acid is formed by the combination of the anhydride with water, and may also be prepared by heating together phosphorus and nitric acid. The reaction with ordinary phosphorus is somewhat violent if the heat be too high, so the amorphous variety is to be preferred ; it possesses the further advantage that being in the form of a powder it offers more surface to the acid. The phosphorus dissolves with the evolution of abundant nitrous fumes ; when all has disappeared, the following reaction will have occurred.

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Nitric acid.}}{10HNO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Phosphoric acid.}}{4H_3PO_4} + \underset{\text{Nitrogen trioxide.}}{5N_2O_3}$$

The liquid is then concentrated by evaporation, until it attains a temperature of 150° C. : the excess of nitric acid is thus dissipated, and there remains behind, on cooling, a solid, glassy mass of what is termed glacial phosphoric acid.

304. **Properties.**— Phosphoric acid is very deliquescent, has a sharp, sour taste, and reddens litmus. The acid here described is tribasic, but three distinct acids are formed by the union of water, in different proportions, with the anhydride. To these acids the following names have been given :—

$$P_2O_5 + H_2O = 2HPO_3 \quad \text{Metaphosphoric acid.}$$
$$P_2O_5 + 3H_2O = 2H_3PO_4 \quad \text{Orthophosphoric acid.}$$
$$P_2O_5 + 2H_2O = H_4P_2O \quad \text{Pyrophosphoric acid.}$$

Each acid may be dissolved in excess of water, and forms its corresponding series of salts.

The tribasic phosphoric acid is also called orthophosphoric acid ('right,' or normal phosphoric acid). If the glacial acid, obtained as previously described, be boiled for some time with water, the liquid contains orthophosphoric acid. The addition of sodium carbonate to this liquid until it has the slightest alkaline reaction to litmus results in the production of disodic phosphate, Na_2HPO_4, which is neutral to litmus. On evaporation this salt may be obtained in large colourless crystals, and forms the sodium phosphate of the shops. If the phosphoric acid solution before this treatment be divided into two equal parts, and the one rendered thus alkaline, and the two then mixed, the resultant salt is the dihydric phosphate, NaH_2PO_4, strongly acid to litmus. The addition of caustic soda to the solution of disodic phosphate results in the crystallising out of the trisodic phosphate, Na_3PO_4, very alkaline in reaction to litmus paper.

If a solution of the disodic phosphate be added to silver nitrate, a canary yellow precipitate of silver phosphate, Ag_3PO_4, is formed. In this case the curious result of the mixture of two neutral liquids producing one having an acid reaction is observed. The reason is that free nitric acid is formed during the reaction :—

$$\underset{\text{Sodium phosphate.}}{Na_2HPO_4} + \underset{\text{Silver nitrate.}}{3AgNO_3} = \underset{\text{Silver phosphate.}}{Ag_3PO_4} + \underset{\text{Sodium nitrate.}}{2NaNO_3} + \underset{\text{Nitric acid.}}{HNO_3}.$$

From lead phosphate precipitated in a similar manner, orthophosphoric acid may be obtained by passing sulphuretted hydrogen through water in which the phosphate is suspended. Lead sulphate is formed, and free phosphoric acid liberated. The liquid is filtered, and by evaporation *in vacuo*, crystals of the ortho-acid, H_3PO_4, obtained. The phosphates, with the exception of those of the alkali metals, are insoluble in water; all are, however, soluble in dilute acids, provided the acid does not precipitate the metal itself.

On heating disodic phosphate to redness, the following change occurs :—

$$\underset{\text{Disodic phosphate.}}{2Na_2HPO_4} = \underset{\text{Sodium pyrophosphate.}}{Na_4P_2O_7} + \underset{\text{Water.}}{H_2O}.$$

This pyrophosphate may be re-dissolved in water, and crystallises out in acicular crystals of the composition

$Na_4P_2O_7,10H_2O$. This next salt yields a white precipitate with silver nitrate of $Ag_4P_2O_7$: it also forms a lead pyrophosphate, $Pb_2P_2O_7$, from which, by the action of sulphuretted hydrogen and subsequent evaporation *in vacuo*, crystals of pyrophosphoric acid, $H_4P_2O_7$, are obtained. The soluble pyrophosphates are stable in solution, but yield ortho-salts on being evaporated.

If, instead of the disodic phosphate, the mono salt, NaH_2PO_4, be heated, sodium metaphosphate is formed. The same change occurs on heating microcosmic salt, $NaHNH_4PO_4$.

$$\underset{\text{Monosodic phosphate.}}{NaH_2PO_4} = \underset{\text{Sodium metaphosphate.}}{NaPO_3} + \underset{\text{Water.}}{H_2O}.$$

$$\underset{\text{Microcosmic salt.}}{NaHNH_4PO_4} = \underset{\text{Sodium metaphosphate.}}{NaPO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Ammonia.}}{NH_3}.$$

This substance in solution in water gives, with silver nitrate, a *white gelatinous* precipitate of silver metaphosphate, $AgPO_3$. The free acid, HPO_3, may be obtained in the same manner as the other varieties by the action of sulphuretted hydrogen on the lead salt. The glacial acid made by the method previously described consists almost entirely of metaphosphoric acid, but by boiling with water may be converted into the ortho variety.

305. Industrial Applications.—Bones, bone-ash, and mineral phosphates are largely employed as manures in order to supply the phosphates required by growing plants. For this purpose they are usually treated with sulphuric acid in order to convert the calcium phosphate into the acid and soluble salt, known as superphosphate of lime, $H_4Ca(PO_4)_2$.

Phosphorus Trioxide.—Formula, P_2O_3 (or P_4O_6). Molecular weight, 108·80, or 217·60.[1]

306. Preparation.—When phosphorus is burned in an insufficient supply of air, this body is formed. The preparation may be easily effected by enclosing a piece of dry phosphorus in a wide glass tube arranged with a small tube corked in at either end. A slow current of air is drawn through the apparatus by an aspirator, and the phosphorus is gently heated; it

[1] Recent investigations, the results of which have been published during the passage of this work through the press, go to show that the formula of this oxide is P_4O_6. See Thorpe on Phosphorous Oxide, *Journal of the Chemical Society*, 1890.

burns with a pale greenish flame, and phosphorus trioxide is deposited in the cooler part of the tube.

307. **Properties.**—This oxide is a white, amorphous powder, with a smell somewhat resembling that of garlic. On being heated in air, it burns to the pentoxide, P_2O_5. It is without action on litmus paper. It is deliquescent, and forms, when acted on by water, phosphorous acid; hence it is commonly regarded as the anhydride of that acid, a view which is not at present universally adopted.

Phosphorous Acid.—Formula, H_2PHO_3. Molecular weight, 81·84.

308. **Preparation.**—When phosphorus is allowed to oxidise in the presence of moist air, phosphorous acid is produced simultaneously with phosphoric and hypophosphoric acids. A preferable way of preparing this acid is by the decomposition of phosphorus trioxide by water. Phosphorus is, for this purpose, melted under water, and a slow stream of chlorine passed into the melting phosphorus: the chloride, as rapidly as formed, is decomposed into phosphorous and hydrochloric acids :—

$$\underset{\text{Phosphorus trichloride.}}{PCl_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphorous acid}}{H_2PHO_3} + \underset{\text{Hydrochloric acid.}}{3HCl.}$$

The reaction must be stopped before the phosphorus has entirely disappeared, in order to prevent the formation of phosphoric acid. The solution is gently evaporated, care being taken that the temperature does not rise above 200° C. The hydrochloric acid is expelled, and deliquescent crystals of phosphorous acid are obtained.

309. **Properties.**—This acid has a garlic-like smell, and when heated is decomposed into phosphoric acid and phosphoretted hydrogen, thus :—

$$\underset{\text{Phosphorous acid.}}{4H_2PHO_3} = \underset{\text{Phosphoric acid.}}{3H_3PO_4} + \underset{\text{Phosphoretted hydrogen.}}{PH_3.}$$

In most of its salts phosphorous acid acts as a diabasic acid, and hence the formula is written H_2PHO_3, the object being to indicate that a part of the hydrogen is not replaceable by a

base. Although it has not as yet been isolated in the anhydrous state, a tribasic phosphite is known, Na_3PO_3, while well-marked phosphites of organic radicals—as ethyl triphosphite, Et_3PO_3—can be obtained as very stable bodies. In strictness, therefore, the formula should be written H_3PO_3. Still, for all practical purposes, so far as inorganic salts are concerned, phosphorous acid yields only two of its hydrogen atoms to be replaced by a metal. The phosphites are easily decomposed by heat, yielding usually various phosphates and evolving hydrogen and phosphoretted hydrogen.

Hypophosphorous Acid.—Formula, HPH_2O_2. Molecular weight, 65·88.

310. **Preparation.**—On heating phosphorus with either calcium, barium, potassium, or sodium hydrates, the hypophosphites are formed, and phosphoretted hydrogen evolved. From barium hypophosphite, $Ba(PH_2O_2)_2$, hypophosphorous acid may be obtained by adding dilute sulphuric acid so long as a precipitate is formed, and then filtering from the barium sulphate. On carefully evaporating, the temperature not being allowed to exceed 105°, a viscous liquid is obtained, which at 0° solidifies into a crystalline mass.

311. **Properties.**—Hypophosphorous acid is possessed of only very feeble acid properties, and forms with bases a series of salts termed hypophosphites. These bodies, as well as the acid itself, are powerful reducing agents, being converted by the absorption of oxygen into phosphites. Sodium hypophosphite, $NaPH_2O_2$, is now largely used as a medicine. The reason for its employment is interesting: phosphorus in certain forms is an essential constituent of brain and nerve-tissue. To supply any deficiency of this body phosphates have been prescribed; but as these represent phosphorus in the highest state of oxidation the medicinal use of phosphates has been compared to feeding a fire with ashes. The hypophosphites, for good or ill effect, introduce phosphorus into the system in a comparatively unoxidised condition.

312. **Hypophosphoric Acid, $H_4P_2O_6$,** is of no practical importance, and cannot here be further discussed.

313. Other Non-Metallic Elements.—There are two other non-metallic elements, selenium and tellurium; and in addition to these many chemists include arsenic among the non-metals.

Selenium.—This element is, in its general properties, very similar to sulphur. It is a hexad in its relations with oxygen, and dyad to hydrogen and the metals. Most of its compounds are similar in constitution to those of sulphur, and usually also in general properties. The element is not sufficiently plentiful to warrant further description.

Tellurium also belongs to the sulphur group, but does not resemble that element so closely as does selenium. Neither are its series of compounds so closely analogous to those of sulphur. It belongs to the class of rare elements.

Arsenic.—This element is practically intermediate between the non-metals and the metals. It, in fact, forms one of a group of elements, the extremes of which are respectively undoubted non-metals and metallic bodies. This group consists of nitrogen, phosphorus, arsenic, antimony, and bismuth. Two of these have already been described; for convenience of description arsenic is placed among the metals, but it should be remembered that its properties are decidedly intermediate between the two classes of bodies.

CHAPTER XXI

THE METALS

314. General Characteristics.—The difference between the metals and non-metals has already been described in the first chapter of this work. The principal points there explained are those relating to the physical characters possessed by the metallic, as distinguished from the non-metallic class of elements. The chemical differences between the two classes may be summed up in the statement that **the oxides of the non-metals are usually either basic or indifferent bodies. The metals form a series of oxides which act as bases**

toward acids. Certain metals, as manganese and chromium, yield several oxides ; of these, those containing the lower proportions of oxygen are basic, while the higher oxides possess acid properties. Arsenic, which is viewed as a pseudo-metal, yields oxides, the lowest of which is acid rather than basic in character: it is this chemical property which leads many chemists to place arsenic among the non-metals. The formation of haloid salts is not of itself sufficient evidence of the metallic nature of an element, because sulphur, phosphorus, and other decided non-metals yield chlorides, bromides, and iodides. The metals are electro-positive in character, being deposited on the negative electrode when their compounds are subjected to electrolysis.

315. Classification of the Metals.—For convenience of description and reference, it is well to arrange the metals into groups, each group consisting of those metals more or less allied to each other. The following is such a classification : the names given at the end of each group in italics are those of the rarer and less important metallic bodies.

Class I. Metals of the Alkalies.—Potassium, Sodium, *Cæsium*, *Rubidium*, *Lithium* (Ammonium).

The metals of this class are usually regarded as monovalent, but yield no single compound of which the molecular weight is known. They are very light, soft bodies, possessing when freshly cut a bright metallic lustre, but tarnishing rapidly, through combination with oxygen. They decompose water at ordinary temperatures, with rapid evolution of hydrogen. Their oxides, hydrates, and carbonates are soluble in water ; the two former are strongly basic. The general formula of their oxides is M'_2O, and of their chlorides $M'Cl$. (The symbol M is used to signify an atom of any metal, and when qualified by a dash or number of dashes, M' or M'', that number is indicative of the valency of the metal referred to.)

Ammonium is usually classed, for purposes of description of its salts, among the alkali metals.

Class II. Metals of the Alkaline Earths.—Calcium, Barium, and Strontium.

These metals are divalent in their more common and stable compounds: there are indications that in some compounds they have a higher valency. They decompose water at all temperatures, with the disengagement of hydrogen. Their oxides unite with water to form hydrates which are more or less soluble; their carbonates are insoluble in water. The oxides have the formula $M''O$ and the chlorides $M''Cl_2$.

Class III. Metals of the Earths.—Aluminium, *Glucinum, Gallium, Yttrium, Erbium, Cerium, Lanthanum, and Didymium.*

The metal aluminium is at least trivalent, and if, as probable, it forms doubly-linked molecules, as Al_2Cl_6, the valency must be as much as four, and is probably six, as in the oxide Al_2O_3. This metal decomposes water at high temperatures. Its oxide and hydrate are insoluble in water, and their basic character much less marked than in the preceding groups.

Class IV. Zinc Group.—Magnesium, Zinc, and Cadmium.

These metals are divalent. They are volatile at high temperatures, and may thus be distilled. They burn with a bright flame when heated in air. At high temperatures they decompose water. Their oxides and chlorides are represented respectively by the formulæ $M''O$ and $M''Cl_2$.

Class V. Iron Group.—Iron, Chromium, Manganese, Cobalt, Nickel, and *Uranium.*

These metals form more than one series of compounds, in which they are respectively di-, tetra-, and hexavalent. They decompose water at a red heat, with evolution of oxygen, but are not themselves volatile at that temperature. Their oxides are represented by the formulæ $M''O, M^{iv}{}_2O_3$, and $M^{vi}O_3$; they form chlorides having the formulæ $M''Cl_2$ and $M^{iv}{}_2Cl_6$. The $M^{vi}O_3$ oxides of this group are acid in character.

Class VI. Tin Group.—Tin, *Titanium, Zirconium, Thorium, Molybdenum, Tungsten, Niobium, Tantalum, Vanadium,* Arsenic (Arsenicum), Antimony, and Bismuth.

Of this group tin is tetravalent, and in several respects is allied to silicon. Its oxide, SnO, is basic, but other of its compounds are somewhat acid in character. These metals, with the exception of arsenic, decompose water at a red heat. The

latter members are usually pentavalent, their oxides and chlorides being represented by $M^{v}{}_2O_5$ and $M^{v}Cl_5$.

Class VII. Copper Group.—Copper, Lead, *Thallium, and Indium*

These metals do not decompose water at any temperature; neither are their oxides decomposed by heat alone. Copper and lead are both divalent in most of their compounds; but lead in some acts as a tetravalent element.

Class VIII. Noble Metals.—Mercury, Silver, Gold, Platinum, *Palladium, Rhodium, Ruthenium, Osmium, and Iridium.*

These metals do not decompose water at any temperature; their oxides are decomposed by heat alone. Mercury is divalent, silver monovalent, gold is trivalent, and platinum is a tetrad. All their oxides are basic in character.

316. Periodic Law.—On arranging the elements in the order of their atomic weights, commencing with hydrogen, 1, and concluding with uranium, 240, it may be observed that elements of somewhat allied character recur at intervals; further, these intervals exhibit considerable regularity, for in a number of cases, starting with any element, each successive eighth one is found to be a member of the same group of allied elements. This remarkable property was first discovered by Newlands, and afterwards independently by Mendeleeff, by whom it was exhaustively examined. The results of this investigation may be summed up in the statement that **the general properties of the elements and also their quantivalence are periodic functions of their atomic weights.** In obedience to this periodic law, Mendeleeff has formulated the following table of elements showing their arrangement into groups as deduced from periodic recurrence.

On examining this table it will be seen that the atomic weights follow consecutively when the elements are read along the lines from left to right. The groups in vertical columns, numbered I, II, III, &c. contain a number of allied elements. Thus, starting from lithium, the alkali metals—sodium, potassium, and others—are included within the same group. The two

	I	II	III	IV	V	VI	VII	VIII			
1	H 1										
2	Li 7·01	Be 9·1	B 11·0	C 12·97	N 14·01	O 15·96	F 19·1				
3	Na 22·99	Mg 24·2	Al 27·3	Si 28·3	P 30·96	S 31·98	Cl 35·37				
4	K 39·04	Ca 39·9	Sc 44·0	Ti 48·0	V 51·2	Cr 52·1	Mn 54·9	Fe 55·9	Ni 58·6	Co 58·7	Cu 63·1
5	(Cu) 63·1	Zn 65·1	Ga 69·8	Ge 72·3	As 74·9	Se 79·0	Br 79·75				
6	Rb 85·2	Sr 87·2	Y 89·0	Zr 90·0	Nb 94·0	Mo 95·6	-- 100	Ru 103·0	Rh 104·1	Pd 106·2	Ag 107·66
7	(Ag) 107·66	Cd 111·9	In 113·4	Sn 118·6	Sb 121·0	Te 125·1	I 126·53				
8	Cs 132·5	Ba 136·8	La 138·0	Ce 139·9	Di 145·0	—	—	—	—	—	—
9	(—)	—	—	—	—	—	—				
10	—	—	Er 166·0	Yb 173·0	Ta 182·0	W 184·0	—	Os 191·0	Ir 192·7	Pt 194·5	Au 196·8
11	(Au) 196·8	Hg 199·8	Tl 205·6	Pb 206·4	Bi 207·5	—	—				
12	—	—	—	Th 231·9	—	U 239	—	—	—	—	—

groups, magnesium, zinc, and cadmium, and also calcium, strontium, and barium, occur in column No. II. Column III. is principally occupied by the rarer metals. In Column IV. we have carbon, silicon, titanium, and tin, all closely allied. The fifth column contains the important group, nitrogen, phosphorus, arsenic, antimony, and bismuth. Oxygen, sulphur, selenium, and tellurium occur in the sixth column; and in the seventh one we have fluorine, chlorine, bromine, and iodine. In the eighth column of the table are included certain elements which do not appear to naturally fall into line in the preceding arrangement. Thus there are the three elements iron, nickel, and cobalt, all much alike and all with very nearly the same atomic weight. So, too, there is the group of ruthenium, rhodium, and palladium, with almost identical atomic weights and similar properties. Falling underneath these, in the same column, is another closely allied group of elements—osmium,

iridium, and platinum—again having very nearly the same atomic weights. The two groups—ruthenium group and osmium group—are closely allied to each other. It would seem that not only is there a similarity between elements whose atomic weights recur at certain definite periods in the list of elements, such as exist in the vertical groups, but also there are cases of allied elements with atomic weights so near as to be almost bracketed equal, and which might be all counted together in one space in Mendeleeff's table. Three metals—copper, silver, and gold—have been placed in this loosely classified eighth group and have also been tentatively entered in the first column, where, probably, their proper place is. It will be noticed that in places in the table spaces exist; these represent instances where no elements are known which fit into these vacant spaces. At the time when this table was first published by Mendeleef, between zinc and arsenic two vacant spaces occurred. With regard to the space next zinc Mendeleef described the hypothetic element by which this space might possibly be occupied; to this element he gave the name *ekaluminium*, and predicated its properties and atomic weight. Some years afterwards the metal gallium was discovered, and agreed almost exactly with Mendeleef's prediction for ekaluminium. The adjoining space in the same line is now filled by germanium, which in common with scandium was also predicted by Mendeleef and both described under the respective names of eka-silicon and eka-boron. The Faraday Lecture 1889, before the Chemical Society, was by Mendeleef on the Periodic Law; he then referred to the possibility of filling other gaps by still undiscovered elements in the following words:—

'I foresee some more new elements, but not with the same certitude as before. I shall give one example, and yet I do not see it quite distinctly. In the series which contains Hg=199·8, Pb=206·4, and Bi=207.5, we can guess the existence (at the place VI—11) of an element analogous to tellurium, which we can describe as dvi-tellurium, Dt, having an atomic weight of 212, and the property of forming the oxide DtO_3. If this element really exists, it ought in the free state to be an easily fusible, crystalline, non-volatile metal of a grey colour, having

a density of about 9·3, capable of giving a dioxide, DtO_2, equally endowed with feeble acid and basic properties. This dioxide must give, on active oxidation, an unstable higher oxide, DtO_3, which should resemble in its properties PbO_2 and Bi_2O_5. Dvi-tellurium hydride, if it be found to exist, will be a less stable compound than even H_2Te. The compounds of dvi-tellurium will be easily reduced, and it will form characteristic definite alloys with other metals.'

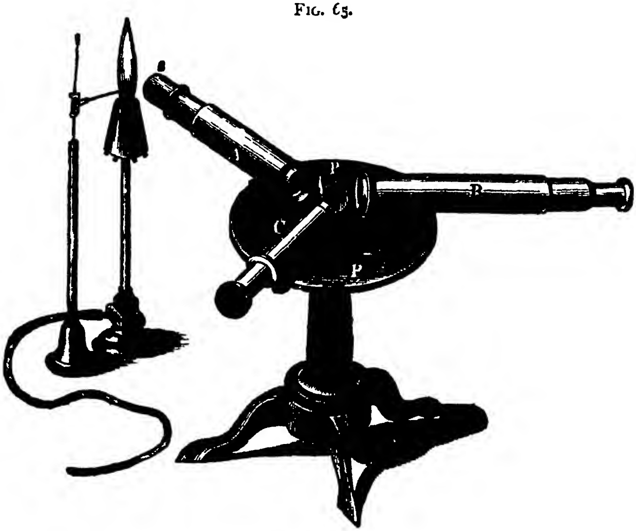
Time will show to what extent these speculations are borne out by chemical discovery. The periodic law has also been of service in determining the atomic weights of elements; thus uranium had formerly the atomic weight of 120 assigned to it, and would then fall between tin and antimony; being out of place there, Mendeleeff proposed to double the atomic weight, and place it in the sixth column among elements to which it is allied. Subsequent determinations of the specific heat of uranium confirmed this view of its atomic weight being 204.

317. **Spectrum Analysis.**—On taking a piece of carbon, lime, or other solid and refractory body, and subjecting it to the action of gradually increasing heat, it after a time becomes self-luminous, emitting a faint red glow; with an increase of temperature the glow increases in brightness and changes through various shades of orange and yellow to white. Lime in this state of brilliant incandescence, as induced by the heat of the oxyhydrogen blowpipe constitutes the well-known lime-light. When a powerful electric current is passed through a pair of contiguous carbon poles they become so intensely heated as to emit light of a violet hue. By passage through a triangular prism, a thin beam of white light, from incandescent lime or other similar source, is resolved into a broad rainbow-coloured band. This is termed, in physics, a spectrum. An examination of the spectrum from a lime-light shows that it is continuous. At the one end there is the deep and scarcely luminous extreme red (this is the end of the spectrum which has been bent the least), while at the other end is the violet, also dying away into non-luminosity. Between them lie all the well-known colours of the spectrum. If, by means of proper

apparatus, the lime-light spectrum be observed from the first appearance of luminosity as the result of heat, it will be found that at first the red end of the spectrum is visible; with an increase of temperature the spectrum extends, until at last, at the highest temperature, the violet extremity is reached. The electric arc light, which is usually more intense than the lime-light, shows a more brilliant violet end to the spectrum. **All solid substances when intensely ignited emit light which affords a continuous spectrum.**

But if, instead of examining the light of solid substances,

FIG. 65.



we turn our attention to that emitted by flames consisting of ignited gases, a totally different appearance is observed. For the purpose of such systematic examination an instrument termed a spectroscope is employed. Fig. 65 shows one of the simpler forms of this apparatus. On the left-hand side is shown the flame of a bunsen lamp, into which a small platinum spoon projects. If a small fragment of common salt be placed in this spoon the flame acquires the well-known yellow sodium tint. The three tubes and glass prism fixed on an iron stand

constitute the spectroscope. The tube A is arranged facing the flame, so that its end B receives the light. At this end, B, is fixed a narrow slit whose width can be regulated at will; a narrow vertical strip of light is thus focussed on the prism *p*, bent on its passage through it and then examined by the telescope B. If a lime-light were in the place of the bunsen flame, a continuous spectrum would be observed through the telescope. But with a bunsen flame treated with sodium, nothing is visible but two narrow bright lines in the yellow part of the spectrum. In the coloured plate given as the frontispiece, No. 1 is the continuous spectrum of such a light as the lime-light; and No. 2 is the spectrum of sodium vapour. **The vapours of different elements when incandescent give in every case intermittent or line spectra,** some of which are very simple, as sodium or hydrogen, while others are somewhat more complicated. But **the spectrum of every element is characteristic of itself.** The sodium lines cannot be shifted in position by any increase of temperature. Neither can any other element be caused to give lines in the same position. Sodium, potassium, strontium, barium, thallium, indium, and other elements yield very characteristic spectra. These may be recognised by the number and position of the lines, which are under the same conditions constant for the same element. Metals which are incapable of volatilisation by the bunsen flame are volatilised by passing an electric spark from a powerful Ruhmkorff coil between wire terminals of the metal under examination. The third tube, C, in the figure contains a small scale, which is also observed simultaneously with the spectrum through the telescope B; the object of this scale is to definitely map out the spectrum and state at what part of it each particular line observed occurs. This instrument is of great service in the laboratory as a means of detecting the presence of many metals, especially the rarer ones in substances under analysis. The examination of a fragment in this manner reveals at once the presence of such metals as may be in the substance, not only thus avoiding very tedious means of separation and recognition but even detecting several which are unrecognisable by other means. Since the application of

the spectroscope to purposes of analysis, the following new elements have been discovered through its instrumentality—cæsium, rubidium, thallium, indium, and gallium.

But not only can spectroscopic analysis be applied to the study of substances we can handle, but also light from any source can thus be examined, and the constitution of the body investigated. Spectra Nos. 5 and 6 on the plate are spectra of hydrogen under respectively high and low pressure; Nos. 8, 9, and 10 are spectra of, respectively, a nebula, star, and the sun's chromosphere: each exhibits the characteristic lines of hydrogen. As these lines are only known to be caused by hydrogen, the obvious inference is that the presence of hydrogen is thus demonstrated in these three astronomical bodies.

We now come to another remarkable type of spectra; the whole of those hitherto mentioned are produced by the *emission* of light from various bodies. Students of physics are well aware that the phenomena of radiation and absorption are reciprocal; substances which are good radiators are good absorbers, and *vice versâ.* Now glowing sodium vapour emits two bright lines in the yellow part of the spectrum: when the light of a continuous spectrum is passed through sodium vapour, it, the vapour, absorbs light of the same character as it ordinarily emits. So, that if when viewing the spectrum of incandescent lime (lime-light) the bunsen flame charged with sodium vapour be interposed, it cuts off the light in the yellow part of the spectrum, and two dark lines appear in exactly the same position as the bright ones of the ordinary emission sodium spectrum. This reversed spectrum is termed an absorption spectrum: **all elementary vapours are competent to produce absorption spectra corresponding with their ordinary emission spectra.** This fact is of enormous interest; for on carefully observing the spectrum of sunlight it is found not to be continuous, but to be crossed by a number of dark lines, which are constant in position and appearance. These lines are named after their discoverer, Fraunhofer's lines. These lines of Fraunhofer exactly coincide with those of the absorption spectra of hydrogen, sodium, and many other elements. The sun is known to consist of an

intensely heated solid or liquid centre, surrounded by an envelope of incandescent vapour. The absorption bands of his spectrum are doubtless due to the elements existing in the gaseous state in the sun's atmosphere. As a result of this method of research, no fewer than thirty-two metals have been detected in the sun.

318. Causes which modify chemical action.—Prior to a detailed description of the metals it will be well to explain some of the causes by which the course of chemical action may be considerably modified or even arrested. An acquaintance with the laws governing the influence of mass, and other such matters, will throw light on many chemical changes otherwise only understood with great difficulty.

319. Influence of surface and solubility.—Chemical activity is greatest with substances in a fine state of division; thus finely divided iron inflames spontaneously on exposure to air. This depends on the fact that the surface is larger compared with the mass when the state of division is extremely fine.

Solubility has already been explained as being necessary for continued chemical action. The concentrated acids are frequently without action on substances when their diluted forms are most active. This is frequently due to the insolubility in the acid of the result of the chemical action.

320. Influence of volatility.—Instances of this have already been given; others will occur in the remainder of this work. Boric and silicic acid are such feeble oxides that they may be displaced at ordinary temperatures by even carbonic acid. At high temperatures, owing to their non-volatility, they displace the strongest volatile acids; thus sulphates may be decomposed by either boric or silicic acid. **At high temperatures fixed substances are usually able to displace those which are volatile, even though the latter may normally possess greater chemical activity.**

321. Influence of mass.—Potassium carbonate is converted into the nitrate and sulphate respectively by the addition

of nitric and sulphuric acids. If these acids be added in excess of the quantity necessary to combine with the whole of the potassium, the question arises, how will the potassium be distributed between the two acids? It is generally admitted that each will be in combination with a portion of the base, but will the addition of more of either of the acids affect the proportion of the base which is in combination with that acid. In other words, does the *mass* of each reagent have any effect on the amount of combination effected by it (in this instance, the production of sulphate or nitrate, as the case may be), *excess* of the reagent being throughout understood? This problem has been investigated both theoretically and practically; with the following as the most important conclusion—**the proportions in which any one body is divided between others in the same solution,** for which it has an attraction (soluble substances being formed in each case) **depends partly upon the strength of the mutual attractions of the components for each other, and partly also upon the mass or relative proportion of each compound which is present in the mixture.**

The following is another effect due to the influence of mass. Through a dilute solution of antimony chloride, $SbCl_3$, the passage of sulphuretted hydrogen causes the precipitation of antimonious sulphide, and liberation of hydrochloric acid. On the other hand, when the sulphide is treated with concentrated hydrochloric acid, decomposition is caused, the chloride being formed and sulphuretted hydrogen liberated. In this case, supposing the antimony chloride to be dissolved in a small quantity of hydrochloric acid, on passing sulphuretted hydrogen it is impossible for the chloride to come in contact with as large a proportion of sulphuretted hydrogen molecules as with those of hydrochloric acid. But if water be gradually added, the passage of sulphuretted hydrogen being continued, the mass of hydrochloric acid in any unit of volume is diminishing, but that of sulphuretted hydrogen is being maintained. When the hydrochloric acid mass is rendered sufficiently small relatively to that of sulphuretted hydrogen, precipitation of antimony sulphide commences.

It has already been pointed out how bodies arrange themselves when three are mixed together, between which two soluble compounds can be formed. When solutions of two soluble salts are mixed, so as to give two bases and two acids, which may form four salts, all of which are soluble, the strong acid usually unites with the strong base, and the weak acid with the weak base, but more or less of each possible combination is probably present. Thus the mixing of sodium bromide and potassium chloride in solution will probably result in the simultaneous existence in the solution of sodium bromide and chloride and potassium bromide and chloride. The proportion of each will depend on the strength of their mutual attraction and the mass of each present in the mixture.

322. Influence of removal of bodies from the arena of chemical action.—We next come to the consideration of the problem of what will occur when on the mixture of two salts, the formation of one insoluble compound is possible. In nearly all such cases, the insoluble compound is formed and precipitated. Thus barium chloride and copper sulphate on being mixed in equivalent quantities result in the precipitation of barium sulphate.

$$\underset{\text{Barium chloride.}}{BaCl_2} + \underset{\text{Copper sulphate.}}{CuSO_4} = \underset{\text{Barium sulphate.}}{BaSO_4} + \underset{\text{Copper chloride.}}{CuCl_2}.$$

Again silver sulphate and hydrochloric acid produce the following reaction, although sulphuric is the stronger acid.

$$\underset{\text{Silver sulphate.}}{Ag_2SO_4} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Silver chloride.}}{2AgCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$

In many of these cases the reaction is not, however, absolutely complete, for if silver nitrate and sodium chloride be mixed in their equivalent proportions, a solution is formed in which the addition of an excess of either salt forms a precipitate of silver chloride. This is due to the fact that minute quantities of both reagents may co-exist in dilute solutions. The addition of excess of either causes the complete precipitation of the other.

There are a number of other problems of very much the same nature as those just described; to the whole of these the following law is generally applicable. **When in any chemical action, the formation is possible of a body which, through insolubility, volatility, or other property, is readily withdrawn from the arena of chemical action, the formation of that body usually occurs.** This is exemplified in the precipitative changes just described. Owing to insolubility, the precipitated body forms and is removed from the sphere of chemical action. This is not in contradiction to the law which causes acids and bases, when mixed, to divide themselves between each other until there is an equilibrium, depending on the relative proportions of chemical attraction and mass, but really is a necessary consequence of it. It has been pointed out that sulphuric and nitric acids will divide potassium between them in solution. Both being in excess, why should they not divide barium in the same way between them, forming a certain proportion of the sulphate and nitrate, instead of entirely forming barium sulphate? The question may be best answered by a supposition regarding the potassium nitrate and sulphate. Suppose the mixture is such that equilibrium is effected by there being equal numbers of molecules, say sixteen, of each salt in the unit volume of solution. Let the sixteen molecules of potassium sulphate suddenly become insoluble and be precipitated, equilibrium no longer exists in the solution; there is at once a tendency for the remaining sixteen molecules of nitrate to divide their potassium and form eight molecules each of nitrate and sulphate; but as soon as formed, this sulphate, if insoluble, would also be precipitated, and thus the number would again be halved until at last one atom only of potassium would remain in solution; assuming that this changed once from the nitric to the sulphuric acid it would at once be precipitated and also removed from the sphere of chemical change. Precisely the same effect is produced by any other agency which tends to remove any one of the bodies which may be formed. If it is volatile at the temperature, any of it which is produced immediately volatilises, the tendency to produce equilibrium

results in the formation of some more of the compound, and that is volatilised in turn. If the temperature be such that one of the salts slowly crystallises out, that change occurs and the salt is gradually formed, until the whole of the body is thus removed. The slow formation of calcium oxalate and other crystalline precipitates is one illustration of this.

The removal from the arena of chemical action may be effected by actual bodily translation of one of the reagents. Thus if ferric oxide be heated in an atmosphere of hydrogen, a small quantity of iron is reduced, with the formation of steam. This reaction does not, however, proceed far, for only a small quantity of water and hot iron can co-exist. But if a current of hydrogen be employed, the whole of the iron may be reduced, because the steam is at once carried away out of the region of attraction of the iron. On the other hand, if iron be heated in an atmosphere of steam, iron oxide and hydrogen are formed; the reaction is not, however, complete, for before its close the iron oxide and steam would react on each other. But in a current of steam the whole of the iron is oxidised, and the oxide thus formed has no opportunity of coming again in contact with hydrogen.

323. Influence of pressure and motion.—When chemical combination is accompanied by diminution in volume, the effect of pressure is found to favour such chemical combination. The most striking examples of the effect of pressure are found in the study of the composition of rock-forming minerals, where enormous pressure results from the weight of superincumbent strata. Experiments have recently been made in which chemical action has been studied under a pressure of 7,000 atmospheres. The result is that not only are powders compressed into coherent solids, but even mixtures of bodies have united to form definite compounds. This is doubtless an effect of the bringing molecules into more intimate contact than is possible at ordinary pressures.

Movement at times favours chemical action; thus certain crystalline substances form more readily in liquids that are being stirred—as, for example, potassium tartrate. On the other

hand, with very unstable bodies, motion, especially when it is of the nature of a sudden shock, may result in their decomposition. Chloride and iodide of nitrogen may be thus decomposed, and it has recently been shown that the shock of the detonation of a fulminating substance may effect the decomposition of carbon disulphide.

324. **Catalytic action.**—There are a number of chemical reactions in which the presence of a certain substance materially assists the reaction, and yet that substance itself remains unchanged at the end of the action in which it has been of service. A very familiar instance is that of the effect of manganese dioxide on potassium chlorate, which in its presence is decomposed at a much lower temperature. In explanation of this phenomenon, Liebig introduced what has been called the catalytic hypothesis. He ingeniously assumed that an unstable body during the act of its decomposition was capable of assisting at least in effecting the decomposition of other bodies. The physical act of the dissociation of the molecule of the one substance, resulted in giving the disruptive blow to the already tottering molecular edifice of another somewhat more stable body. The fermentative action of yeast was one of those changes thus explained by Liebig, yeast being the unstable substance which in its decomposition overthrew likewise the sugar molecule, the *débris* of the latter being alcohol and carbon dioxide. This hypothesis was overthrown when yeast was shown to be an organism, which decomposed sugar as one of its vital functions. Similarly the catalytic hypothesis is being abandoned in the case of other somewhat obscure chemical reactions. Thus in the case of manganese dioxide, there is every probability that certain more highly oxidised compounds of manganese are formed from the potassium chlorate, which again undergo decomposition, and thus these bodies act as 'carriers' of oxygen from the chlorate to the free state. The function of nitric oxide as an oxygen-carrier in the manufacture of sulphuric acid has already been explained. If the formation and reduction of the peroxide happened to be chemical changes which were difficult of detection, this would

be a very striking example of so-called catalytic action. The phrase catalytic action may generally be interpreted as meaning an obscure chemical change imperfectly understood.

325. **Influence of temperature.**—In most cases there is a range of temperature within which chemical action between bodies occurs most readily. Thus at ordinary temperatures, oxygen and mercury do not unite; but at about 370° C. the two combine to form mercuric oxide, which at a higher temperature is again decomposed. It is only therefore within a comparatively narrow limit that combination of these elements is practicable. All bodies at a sufficiently low temperature seem unable to combine; on the other hand, provided the temperature be sufficiently high, dissociation of all compounds would most probably occur.

CHAPTER XXII

THE ALKALI METALS

Potassium—Symbol, K. Atomic weight, 39·1. Specific gravity, 0·865. Melting-point, 62·5°C.

326. **Occurrence.**—This metal does not occur in the free state, but is a widely diffused constituent of granitic and similar rocks, in which it is found as a component of insoluble silicates such as felspar and mica.

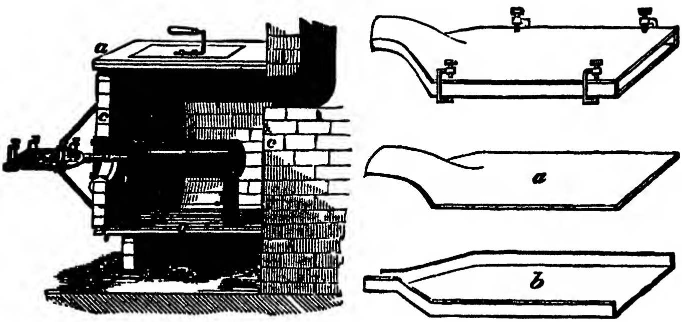
327. **Preparation.**—Potassium was first prepared by the electrolysis of fused potassium hydrate. The metal may also be obtained by reducing potassium hydrate with iron filings at a white heat.

328. **Manufacture.**—Potassium is now almost universally obtained by reducing its carbonate by the action of carbon at high temperatures. For this purpose an intimate admixture of the carbonate and carbon is obtained by heating such a salt as potassium tartrate. (Many organic salts are thus decomposed with evolution of volatile matters, leaving a residue of the

metal as carbonate, and the excess of free carbon which was combined in the salt.) The mixed material is placed in a retort, which conveniently may consist of one of the iron bottles (*b*, fig. 66), in which mercury is imported.

The mercury bottle is placed in a furnace, *c c*; to its neck is attached a short iron tube, *d*, by which it is connected with a shallow receiver, *e*. This receiver is shown on a larger scale on

FIG. 66.



the right-hand side of the figure; it consists of two thin iron plates which are fastened together with screw clamps. The receiver is made in this fashion to permit of the ready cooling of the potassium vapour. On heating the retort to whiteness, the following change occurs :—

K_2CO_3	+	2C	=	2K	+	3CO
Potassium carbonate.		Carbon.		Potassium.		Carbon monoxide

The potassium condenses in the liquid form in the receiver and after solidification is transferred to a vessel containing mineral naphtha. Potassium combines readily with carbon monoxide to form an explosive compound, hence it is necessary to re-distil it and thus free the metal from this body.

329. **Properties.**—Potassium is a silvery-white metal, which, however, tarnishes immediately on its surface being exposed to the atmosphere. At ordinary temperatures it is soft, and two cut surfaces may, by a little pressure, be welded together. At 0° C. it becomes crystalline and brittle. The melting-

point of this metal is 62·5°, and at a red heat it boils, with the production of a green vapour. Potassium burns in air or oxygen, with the production of a violet-coloured flame. This metal has such an attraction for oxygen as to cause it to decompose water, and most other liquid and gaseous oxygen-compounds. It is the most electropositive element known, with the exception of the rare metals cæsium and rubidium. The attraction of potassium for oxygen necessitates its being kept under an oxygen-free fluid such as naphtha (a compound of carbon and hydrogen). Potassium combines readily with chlorine and the other halogens. It is one of the most powerful reducing agents known.

Metallic potassium is but little used in the industries, as sodium possesses much the same properties in a far more manageable form.

The following is a description of the most important potassium compounds :—

330. **Potassium Chloride, KCl.**—This salt occurs in combination with magnesium chloride at Stassfurt, Germany, where it forms large beds, deposited over a stratum of rock salt. The chloride may also be produced by the action of hydrochloric acid on the carbonate. Potassium chloride forms cubical crystals, is soluble in water, and very deliquescent. The salt is employed in the preparation of potassium alum, $K_2Al_2(So_4)_4$.

331. **Potassium Bromide, KBr.**—This salt may be prepared by decolourising bromine by the addition of a solution of potassium hydrate, evaporating, and igniting to decompose the bromate thus formed. The salt is used both in medicine and for photographic purposes.

332. **Potassium Iodide, KI.**—This salt is prepared in a similar manner to the bromide. It is very soluble in water; and its solution is a ready solvent for iodine. Potassium iodide is largely employed for medicinal purposes.

The halogen salts of potassium are devoid of water of crystallisation. When the crystals of any compound contain water, the fact will be indicated in the formula placed at the head of paragraph.

333. Potassium Oxides.—Two oxides of potassium are known, K_2O, and KO_2, the latter being formed when the metal is heated in dry air or oxygen. The peroxide, KO_2, on being fused with potassium, yields the normal oxide, K_2O. These bodies have a great attraction for water, with which they combine, yielding the hydroxide or hydrate, KHO, known also as caustic potash. (The decomposition of the peroxide by water is accompanied by evolution of free oxygen.)

334. Potassium Hydrate, KHO.—The great readiness with which the oxide combines with water causes this, the hydrated oxide, to be by far the more familiar form of the base.

Preparation.—On dropping potassium into water potassium hydrate is produced and dissolved: from this solution it may be obtained by evaporation.

The more usual method of preparation depends on the fact that potassium carbonate is decomposed by calcium hydrate, according to the following equation:—

$$\underset{\text{Potassium carbonate.}}{K_2CO_3} + \underset{\text{Calcium hydrate.}}{Ca(HO)_2} = \underset{\text{Potassium hydrate.}}{2KHO} + \underset{\text{Calcium carbonate.}}{CaCO_3}.$$

To a solution of potassium carbonate, lime is added, until, after the subsidence of the insoluble calcium carbonate, the clear liquid gives no effervescence on treatment with hydrochloric acid. This shows that potassium carbonate no longer remains in solution. The clear supernatant liquid is decanted and evaporated in an iron or silver basin, and then heated nearly to redness. The resultant liquid is either poured on to a slab and allowed to solidify, or into cylindrical moulds and thus cast into sticks.

Properties.—Potassium hydrate is a yellowish or greyish-white substance having a great attraction for both water and carbon dioxide. The solution feels slippery to the touch, and possesses great detergent (cleansing) properties. These are largely due to its solvent power on fats and oils, with which it combines to form the substances known as *soaps*. Potassium hydrate dissolves albuminous matters, and thus exercises a solvent action on the skin, which causes it to be a most powerful caustic. A concentrated solution of potash slowly attacks glass

and so frequently 'sets' the stoppers of bottles in which it is stored. It is almost the most powerful base known, and neutralises all acids. The following table shows the strength of caustic potash solution of various densities :—

Density	KHO in 100 parts	Density	KHO in 100 parts	Density	KHO in 100 parts
1·036	5	1·288	30	1·604	55
1·077	10	1·349	35	1·667	60
1·124	15	1·411	40	1·729	65
1·175	20	1·475	45	1·790	70
1·230	25	1·539	50		

Potassium hydrate is used in the laboratory as a reagent, and also for the drying of gases and the absorption of carbon dioxide. Soft soap is manufactured from a solution of caustic potash.

335. **Potassium Carbonate, K_2CO_3.**—On the application of heat, organic substances containing potassium leave a residue of mineral matter, in which the potassium occurs as the carbonate. Hence, on the burning of wood, the ashes are found to contain potassium carbonate in large quantities.

Preparation.—Formerly, wood-ashes were practically the only source of this salt. Wood is collected in piles and burned. The ash is treated with water, and the soluble portion separated and evaporated to dryness; the residue constitutes the 'potashes' of commerce. On re-dissolving 'potashes' in a small quantity of water, then separating by filtration from the less soluble salts, and once more evaporating and calcining, a purer form of the carbonate is obtained, known as 'pearl-ash.'

At present, potassium carbonate is being obtained from the German and other potassium chloride deposits, by the same process as that employed for the manufacture of sodium carbonate, and described under 'Sodium Carbonate.'

Pure potassium carbonate is generally obtained from one of the organic salts, acid potassium tartrate being most convenient. This is purified by crystallisation and then heated to redness in a platinum vessel, when a mixture of the carbonate and char-

coal remains. On treatment with water, filtration, and evaporation, pure potassium carbonate remains.

Properties.—Potassium carbonate is a white, very soluble, and deliquescent salt. It is insoluble in alcohol, and so is frequently used in order to remove water from that substance. Dry potassium carbonate and the spirit are shaken up together; after a time the carbonate falls to the bottom, carrying with it the water and forming there an oily-looking layer. Potassium carbonate has a strongly alkaline reaction and, like the hydrate, is a powerful detergent. It melts at a red heat and then possesses the property of attacking silica and silicates; its carbon dioxide is evolved and potassium silicate formed.

Industrial Applications.—Potassium carbonate is one of the most important of the potassium salts; it is employed in the manufacture of glass, soft soap, and for the preparation of many other of the potassium compounds.

Acid Potassium Carbonate, $KHCO_3$.—This body, termed also bicarbonate of potash, is formed by passing carbon dioxide through a concentrated solution of the normal carbonate. Being much less soluble, it separates out as a white powder. The hydric carbonate is neutral to litmus paper, and evolves carbon dioxide on being heated.

336. **Potassium Sulphate, K_2SO_4.**—This salt is formed by the action of sulphuric acid on the chloride. It is soluble in water to the extent of one part in twelve.

Acid Potassium Sulphate, $KHSO_4$.—This salt is much more soluble than the normal sulphate; it occurs as a bye-product in the manufacture of nitric acid from potassium nitrate.

337. **Potassium Nitrate, KNO_3.**—This very important salt of potassium, known also as nitre or saltpetre, occurs as an efflorescence of small acicular crystals on soils charged with organic matter, especially in warm climates. It is thus produced by a process of oxidation of nitrogeneous matter, usually of animal origin, which the soil contains. This formation of potassium nitrate is termed 'nitrification,' and is a specific result of the action of certain species of *bacteria*.

Preparation.—In addition to the collection of nitre thus

naturally formed, its production is artificially cultivated by the employment of what are called nitre plantations. A bed of clay of non-porous soil being chosen, there is built on it a mound of loose chalky soil; this is kept moistened with urine and liquid stable manure. Gradually the organic matter is oxidised and nitric acid formed, which in part occurs in combination with the potassium also present, and in part as calcium nitrate. These changes are found to prevail more readily in the soil of old plantations than of new—a consequence, doubtless, of the former being charged with the nitrifying organism which at first is comparatively scarce in the new soil. Periodically, the soil is lixiviated and the aqueous solution of nitrates thus obtained is treated with potash; this precipitates calcium carbonate, and nitre remains in solution. Crude saltpetre is obtained from this liquid by crystallisation. Its purification is effected by dissolving the salt in as little hot water as possible: nitre, being very soluble, is thus separated from sodium chloride and other impurities which remain undissolved. This liquid is then allowed to crystallise; if small crystals are required, it is continually stirred while cooling; if large, the liquid is allowed to remain at rest.

Properties.—Potassium nitrate readily crystallises in long hexagonal prisms, which are not deliquescent, but which dissolve readily in cold and still more so in hot water. The salt melts at 358° C. without decomposition, but on being more strongly heated is reduced to the nitrite with the evolution of oxygen. Owing to the readiness with which oxygen is evolved, potassium nitrate constitutes a most valuable oxidising agent: paper dipped in its solution and allowed to dry burns readily away with a smouldering flame and is known as *touch-paper*. When a little is mixed with charcoal and the two heated, deflagration occurs. The principal uses made of nitre are in the preparation of nitric acid and the manufacture of gunpowder.

338. Gunpowder.—This very familiar body is a mixture of nitre, charcoal, and sulphur. It takes fire readily, and burns with explosion. The oxygen necessary for the combustion of the charcoal and sulphur is supplied by the nitre; hence this

mixture can burn not only in air, but also under water, or in any air-free cavity. The explosion of gunpowder is used in guns for the propulsion of the bullet or other charge. A special form of gunpowder is also used in quarries and mines for 'blasting' rocks asunder : holes are bored in the rock and filled with the powder, which is carefully rammed down, and then fired by means of a safety-fuse. With the explosion, the rock should be split up into comparatively large masses. Gunpowder somewhat varies in composition, but approaches approximately to a mixture of one atom of sulphur and three atoms of carbon to two molecules of nitre, as illustrated in the following table :—

Nitre	$2KNO_3$	=201·86	=74·8 per cent.
Sulphur	S	31·98	11·9 „ „
Charcoal	3C	35·91	13·3 „ „
		269·75	100·0

The gaseous products of combustion consist principally of carbon dioxide and nitrogen ; while the potassium and sulphur, combine with a portion of the oxygen, and thus produce potassium sulphate ; considerable quantities of potassium carbonate are also formed. These latter bodies constitute the white smoke caused by the explosion of gunpowder. The reaction is complicated, and is affected by the proportions of ingredients in the powder used, and the conditions under which it is exploded.

339. **Other Potassium Salts.**—Among these may be mentioned the potassium sulphides, K_2S_2 and others. It is doubtful whether the normal sulphide, K_2S, can exist. Potassium combines with sulphur in a number of different proportions, forming a series of polysulphides from K_2S_2 up to K_2S_5. These bodies are soluble in water, and on treatment with an acid, evolve sulphuretted hydrogen and deposit sulphur. Potassium hydrosulphide, KHS, is obtained by saturating a solution of the hydrate with sulphuretted hydrogen.

Potassium chlorate has been already described.

Potassium silicate is produced by fusing silica together with potassium carbonate. This salt is now being used in the manufacture of soap.

Sodium.—Symbol, Na. Atomic weight, 22·99. Specific gravity, 0·972. Melting-point, 97·6° C.

340. **Occurrence.**—Sodium in combination occurs plentifully in nature, being a constituent of many minerals. It is, however, principally found as sodium chloride in sea-water, and also as such in the enormous beds of rock salt situate and worked in Cheshire and elsewhere.

341. **Preparation.**—Sodium is prepared by methods similar to those adopted in the case of potassium; thus the electrolysis of the fused hydrate yields the metal, although somewhat less readily than potassium is liberated in the same manner.

342. **Manufacture.**—The carbonate of sodium, like that of potassium, is decomposed by carbon at a white heat, and in this manner sodium is manufactured. Ordinary soda-ash (a commercial carbonate), powdered charcoal, or small coal, and chalk are ground together into a very fine powder This mixture is made into a paste, dried, broken into small lumps, and introduced into an iron retort coated with clay on the outside, and provided with a door at each end. The retorts are arranged in series in a furnace, so that both ends project; the doors are securely fastened to the open ends, and the sodium vapour condenses in a receiver arranged for its reception, and similar to that employed for potassium; from this receiver the liquid metal drops into vessels of petroleum placed underneath for that purpose. It is melted under petroleum and cast into bars.

The object of the chalk is to prevent the heated mixture from becoming sufficiently liquid to permit of the separation of the charcoal and sodium carbonate. Sodium does not form an explosive compound with carbon monoxide, and so its preparation is far less dangerous than that of potassium.

343. **Properties.**—Sodium is a metal exhibiting when freshly cut a silvery white lustre; its melting-point is higher than that of potassium, but its boiling-point is somewhat lower. Sodium and potassium in their properties, and also those of

their compounds, closely resemble each other. The former metal is very nearly, but not quite, as active a chemical agent as potassium, and is extensively employed as a reducing agent. In order to preserve it from oxidation, sodium is usually kept underneath mineral naphtha, or some other liquid hydrocarbon. Sodium decomposes cold water, with evolution of hydrogen, but does not usually take fire.

344. Industrial Applications.—Sodium is largely used in the preparation of metallic magnesium and aluminium. The quantities manufactured for this purpose cause sodium to be a comparatively cheap substance.

345. Sodium Chloride, NaCl.—This substance, known also as common salt, is found plentifully in nature, both in the solid state in beds of rock salt and in solution in sea-water. Smaller quantities of sodium are found in the water of rivers, while traces are almost everywhere present in the air.

Preparation.—Pure sodium chloride is prepared by passing hydrochloric acid gas into a saturated solution of common salt. As the solution becomes acid the sodium chloride is deposited, and magnesium chloride and other impurities remain in solution.

Extraction.—Salt is obtained by evaporation of sea-water, from which it crystallises, leaving behind the mother liquor or bittern from which bromine is extracted. More frequently in this country salt is obtained from the various rock salt deposits; water is allowed to flow through these, after which it is pumped to the surface as a saturated brine and then separated by crystallisation or evaporation. Large quantities of rock salt are also raised in the solid state.

Properties.—Sodium chloride is a soluble substance with a pleasant saline taste. It occurs in crystalline masses, sometimes containing well-defined colourless cubical crystals of considerable size. Salt melts at a red heat, and at high temperatures may be volatilised. One part of salt is dissolved by about three parts of cold water, and slightly less of hot water. The solution, known as brine, is a very powerful antiseptic.

Industrial Applications.—Salt is largely used as a con-

diment, and also for the preservation of meat. For this purpose it is now being superseded by Appert's process of preservation, which consists of heating the meat so as to destroy all germs of putrefaction, and then hermetically sealing in tins. All tinned foods are prepared in this manner. Salt is also used for the purpose of producing a glaze on common earthenware; and as a source of the other sodium salts, chief among which is sodium sulphate, which in its turn becomes the source of the carbonate and hydrate.

346. Sodium Sulphate, $Na_2SO_4,10H_2O$.—Sodium sulphate is found native in the mineral Thénardite; but almost all which finds its way into commerce is prepared from the chloride.

Preparation.— In the preparation of hydrochloric acid, by the action of sulphuric acid on sodium chloride, the acid sodium sulphate is obtained; at a higher temperature, normal sodium sulphite is formed according to the reaction :—

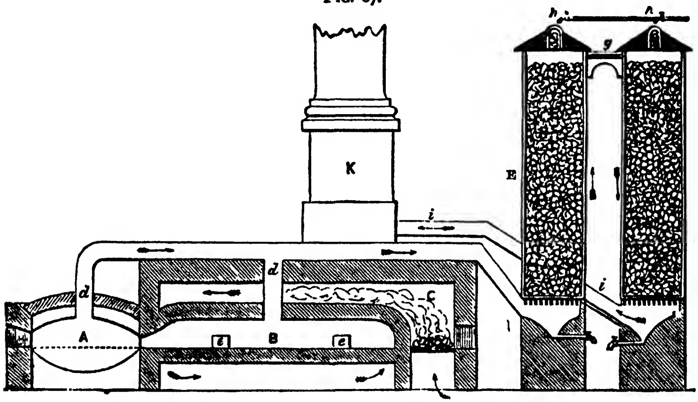
$$\underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sodium ~~sulphite~~}}{Na_2SO_4} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

Manufacture.—The manufacture of sodium sulphate is one step in a train of manufacturing operations which, taken together, constitute the most important chemical industry of the kingdom. The operation is conducted in a reverberatory furnace, such as is shown in fig. 67, in which A is a cast-iron pan known as the decomposer; into this a charge of about 5 cwt. of salt is introduced, and then rather less than that weight of the brown sulphuric acid of commerce. This is subjected to a gentle heat by the gases which reach it through the flue from the furnace C. Hydrochloric acid vapours escape and are conducted by *d* to the coke towers E, F; through these a stream of water trickles down and thus dissolves the hydrochloric acid, which collects at the bottom and is there drawn off, and constitutes the crude hydrochloric acid of commerce. At the bottom of the second tower, F, the fumes are carried by means of the pipe *i* into the smoke-stack, K. In this iron pan A, the sulphuric acid is converted into the acid sodium sulphate, the following change having occurred :—

$$\underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Acid sodium sulphate.}}{NaHSO_4} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

The still pasty mass is next transferred to that portion of the furnace marked B. Here it is exposed to a considerably higher temperature, and the chemical change is completed, normal sodium sulphate, in the anhydrous condition, being

FIG. 67.



formed. The hydrochloric acid fumes escape through *d* to the coke-towers. The finished sodium sulphate is then removed from the furnace and is known technically as 'salt-cake.' In manufacturing operations, as soon as the one charge has undergone the first half of the decomposition in the part of the furnace A, its place is taken by a fresh charge, so that both sections of the furnace are in continuous work.

Properties.—On solution in water, the anhydrous sulphate may be obtained by crystallisation in the form of four-sided prisms of $Na_2SO_4,10H_2O$. These crystals lose their water with great readiness on exposure to air. The salt was formerly used in medicine as a purgative, being known as Glauber's salt. Sodium sulphate is one of those bodies which, when dissolved in water, exhibit in a marked degree the property of supersaturation. If a saturated solution be prepared with boiling water, and then allowed to cool in chemically clean vessels, it

falls to the temperature of the atmosphere without depositing any of the salt. On then adding a single crystal of the sulphate, the solution crystallises throughout its whole mass, with considerable rise in temperature.

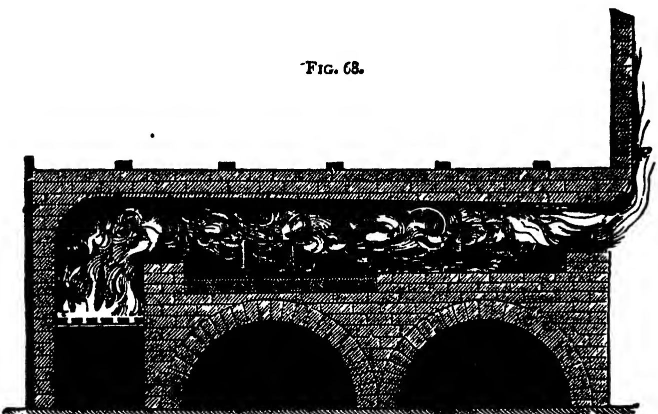
347. Sodium Carbonate, Na_2CO_3, $10H_2O$.—This salt was formerly obtained from the ash of sea plants in much the same way as potassium carbonate is obtained from wood ashes. At present by far the greatest quantity is produced from sodium sulphate (salt-cake) by what is known as Leblanc's process.

Manufacture.—On roasting together sodium sulphate, charcoal or coal, and chalk, the following reaction occurs.

$$\underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Carbon.}}{C} = \underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Calcium sulphide.}}{CaS} + \underset{\text{Carbon monoxide.}}{4CO.}$$

This operation may be viewed as consisting first of the deoxidation of the sodium sulphate into sulphide by the carbon, and then an interchange, by which the sodium becomes converted to a carbonate, at the expense of the calcium, which combines with the sulphur to form a sulphide.

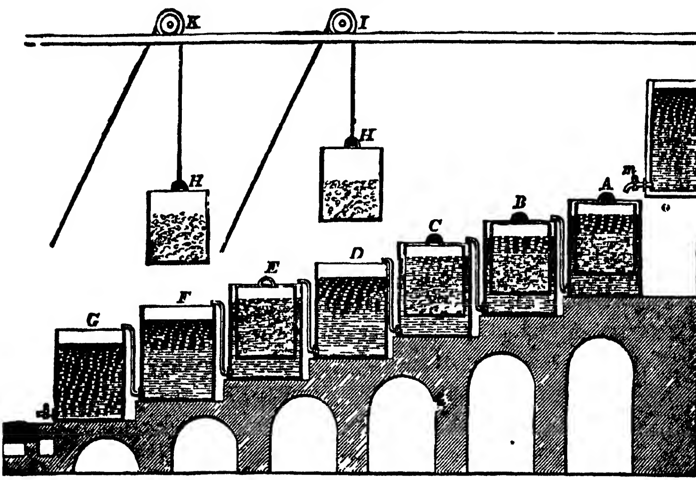
FIG. 68.



This change is effected in a furnace such as that shown in

fig. 68. A charge of about $2\frac{1}{2}$ cwt. of the mixture, in the proportion of three parts salt-cake, three parts chalk, and two parts of coal, is introduced into the furnace through the door E, and rests on the higher part of the floor C. This melts, and rapidly evolves carbon monoxide; after a time it is raked into the lower part of the floor B, and allowed then to settle into a state of tranquil fusion. Meantime another charge is placed on the first part of the hearth, and so the two processes go on simultaneously. The product of the completed reaction is raked out and allowed to cool. It contains excess of coal

FIG 69.



and lime, which at the temperature has been partly converted into quicklime; from its black colour this body is technically termed 'black ash.'

The next stage of the manufacture is the lixiviation of the black ash, in order to extract the sodium carbonate. For this purpose an arrangement of vats, such as is shown in fig. 69, is adopted. A series of vats, A—G, are arranged each slightly above the other, so that the water from each one of the series may flow into that beneath it. The first vat is fed continuously with water from the tank L. The black ash is put into perforated

sheet-iron vessels H, H, which just fit into the vats. As brought from the furnace, the black ash is first dropped into the vat G, and then after a time removed and placed in F, and its place in G taken by a fresh vessel of black ash. Finally, the almost exhausted ash arrives at the vat A, where it is finally washed in pure water. In this way the lixiviation is conducted with the least possible consumption of water. The solution thus obtained usually contains a certain proportion of caustic soda, NaHO, produced by the action of the calcium hydrate; it is next evaporated in vessels arranged for that purpose over the black-ash furnaces, and heated by their waste heat. During the evaporation, the sodium carbonate crystallises out, and is removed in perforated iron ladles. The residue is either carbonated by passage through coke towers, through which ascend carbon dioxide gas, and then evaporated to dryness; or it is treated as subsequently described and sent into the market as sodium hydrate. The sodium carbonate obtained by this process is termed 'soda ash.'

The insoluble matter remaining after lixiviation of the black ash is known as soda waste, and is the *bête noire* of the soda-manufacturing districts. Enormous heaps of this material accumulate in the neighbourhood of alkali-works, and become a source of serious unpleasantness, owing to their evolving sulphuretted hydrogen as the result of the decomposition of the calcium sulphide present. In addition, these heaps represent a considerable source of loss of material, as the whole of the sulphur employed throughout the manufacture finds its way here. Various methods have been proposed for the recovery of sulphur from this alkali waste, but hitherto they have only met with partial success.

Ammonia process.—Notwithstanding many attempts at improvement, the Leblanc process has, until recently, held the field against all comers as the most economical method of manufacturing sodium carbonate. Recently, however, another method has been introduced under the name of the 'ammonia process,' which already has considerably realised its promises of success. This method of sodium carbonate manufacture depends on the reaction expressed in the following equation:—

$$\underset{\text{Sodium chloride.}}{NaCl} + \underset{\text{Hydric ammonium carbonate.}}{AmHCO_3} = \underset{\text{Ammonium chloride.}}{AmCl} + \underset{\text{Hydric sodium carbonate.}}{NaHCO_3}.$$

A solution of salt is first prepared, and into this gaseous ammonia is passed until the solution contains approximately a molecule of ammonia for each molecule of sodium chloride present. The quantity of ammonia is gauged by the diminution in density of the solution. Carbon dioxide gas is prepared by heating calcium carbonate in a current of steam, and this is passed into the solution until saturated. The acid carbonate of soda is only slightly soluble, and separates in the form of small crystals which are collected and dried by a centrifrugal drier. The acid carbonate is washed in a small quantity of water and sold as such, or is heated and thus converted into the normal carbonate. The carbon dioxide thus evolved is used in a repetition of the reaction. The mother-liquor contains ammonium chloride, from which the ammonia is separated by treatment with lime, and then used again. It will be noticed that this is a 'wet' method of preparation, and that the formation of the salt is due to that property referred to in the preceding chapter, namely that when two salts, by acting on one another, may produce a compound which is easily removed through sparing solubility, that compound is usually formed.

Pure sodium carbonate may be obtained by heating the bicarbonate, or on the ignition of sodium oxalate, and extraction of the carbonate with water.

Properties.—On dissolving dry sodium carbonate, such as soda ash, in water, it readily recrystallises in prisms containing 10 molecules of water of crystallisation. The salt thus obtained is very soluble in cold water, and on being heated, dissolves in its water of crystallisation. On this being driven off by continued heat, a white spongy mass of the anhydrous carbonate remains; this melts at a red heat, and in that form readily attacks silica and silicates, being decomposed with the liberation of carbon dioxide. The solution has a nauseous, burning taste, and is strongly alkaline to litmus paper. This salt differs from potassium carbonate in readily giving up its

water of crystallisation, losing weight on being kept, while the latter is strongly deliquescent in character. Sodium carbonate possesses marked detergent properties.

Industrial Applications.—Sodium carbonate is most extensively used in the arts. Large quantities are employed in the manufacture of glass and of soap. It forms the starting point in the preparation of almost all other sodium salts. Except in some few instances, salts of sodium are preferred to those of potassium, because of their greater cheapness.

348. Acid Sodium Carbonate, $NaHCO_3$.—This body, called also sodium bicarbonate, or bicarbonate of soda, may be obtained direct from the chloride by the ammonia process; or may be prepared by passing a current of carbon dioxide gas through a concentrated solution of the normal carbonate. The bicarbonate is also manufactured by passing carbon dioxide gas over moistened crystals of sodium carbonate contained in wooden trays. The bicarbonate is soluble in 12 parts of water; its solution is not so burning to the taste as that of the normal carbonate, and it is neutral to litmus. On prolonged boiling with water, the bicarbonate loses its additional carbon dioxide, which is also evolved on heating the dry salt to 100° C. This body is largely used in medicine, and forms the carbon-dioxide-supplying basis of most effervescent drinks, and also baking powders.

349. Sodium Hydrate, NaHO.—Like potassium hydrate, this body is far too energetic a compound to be found in a free state in nature. It is also known as sodium hydroxide or caustic soda.

Preparation.—The simplest method of preparing this body is by the action of metallic sodium on water. When the hydrate is required in the purest possible form for purposes of analysis, this method is often adopted. A silver basin is floated in a vessel of ice-cold water, and has a small quantity of pure water poured in it. Clean pieces of sodium are dropped in, one at a time; an energetic action ensues, which is allowed to finish before another piece is added. Finally, the solution is evaporated and heated to about 200° C.;

and the resulting hydrate cast into sticks and allowed to cool.

Manufacture.— On the manufacturing scale, sodium hydrate is prepared from the residual liquor, known technically as 'red liquor,' owing to its colour, which remains after the removal of the sodium carbonate from the solution yielded by the lixiviation of 'black ash,' and which liquor, it will be remembered, contains caustic soda as the result of the action of the lime present. Air under pressure is forced through the hot 'red liquor,' and afterwards sodium nitrate is added. These serve as oxidising agents, and precipitate the iron, which is present, as oxide, and oxidise the sulphides to sulphates. The liquor is evaporated down, and finally raised to nearly a red heat, after which it is allowed to cool and is ladled out into iron drums, in which it solidifies.

The ordinary carbonate may be causticised by the addition of calcium hydrate in a manner similar to that employed in the production of caustic potash; the solution is then evaporated to dryness.

Properties.— In appearance and properties, sodium hydrate is very similar to that of potassium. It is a white, powerfully caustic, and alkaline body, and is very soluble in water, to which, like caustic potash, it imparts a greasy feel. Sodium hydrate has a great attraction for carbon dioxide, which gas it absorbs with avidity. The following table gives the strength of caustic soda solutions of various densities.

Density	NaHO in 100 parts	Density	NaHO in 100 parts	Density	NaHO in 100 parts
1·059	5	1·279	25	1·488	45
1·115	10	1·332	30	1·540	50
1·170	15	1·384	35	1·591	55
1·225	20	1·437	40	1·643	60

Industrial Applications.—Sodium hydrate is employed in soap-making, also for cleansing purposes in dye-works, and for purifying carbolic acid, petroleum, and other substances.

350. Sodium Oxides.—The most important of these is

Na_2O, which is obtained on burning the metal in dry air. It is very deliquescent, combining with water to form the hydrate $NaHO$. The dioxide, Na_2O_2, is produced when sodium is ignited in an excess of oxygen.

351. **Sodium Sulphite, $Na_2SO_3,10H_2O$.**—This body is prepared by passing sulphur dioxide, produced by the burning of sulphur, into a solution of the carbonate. The hydric sulphite, $KHSO_3$ is first formed, and to this a quantity of sodium carbonate solution, equal to that first taken, is added. Sodium sulphite crystallises out in colourless efflorescent crystals. This salt is used for the removal of the last traces of chlorine from bleached goods, being known as 'antichlor.' It is also employed as an antiseptic in the preservation of beer and other fermented liquors.

352. **Sodium Thiosulphate, $Na_2S_2O_3$.**—This body, commercially known as hyposulphite of soda, is prepared by digesting sodium sulphite with sulphur. It is largely used by photographers as a solvent for the haloid salts of silver.

353. **Sodium Nitrate, $NaNO_3$.**—This body is found in large deposits in various parts of South America. It forms rhombohedral crystals, approximating to cubes in shape, and hence has received the name 'cubic nitre.' It is slightly deliquescent, and hence, though very similar in properties, cannot be used instead of potassium nitrate in the manufacture of gunpowder. For that purpose it is converted into potassium nitrate by the addition of potassium chloride, and subsequent crystallisation. It is used as a manure and also as a source of nitric acid.

354. **Sodium Silicates.**—A number of silicates of sodium have been prepared by fusing together sodium carbonate and silica in different proportions. With excess of sodium carbonate, a silicate is formed having the composition $Na_2Si_4O_9$. This, when prepared, has a glassy appearance, and is soluble in water, hence it has received the name of water-glass, or soluble glass. This substance possesses several valuable properties, among which is that of combining with the calcium of a soluble

salt to form an insoluble silicate. Use is made of this property in the preservative treatment of certain limestones used for building properties. The stone-work is first treated with the water-glass in solution, and then with calcium chloride. The insoluble calcium silicate formed on the surface protects the stone from atmospheric degradation. A similar application of sodium silicate is that of the manufacture of artificial stone. Water-glass is employed as a mordant in calico-printing and also as an alkaline constituent of soap.

355. Other Sodium Salts.—The great basic energy of sodium oxide causes it to form salts with practically every known acid; but most of these cannot receive description within the limits of this work. The borate, $Na_2B_4O_7$ (borax), and the phosphates have already been described in dealing with their respective acids.

Ammonium.—Formula NH_4 or Am.

356. Occurrence.—The hypothetic constitution of this body has already been explained; it is inserted here because the salts of this compound so closely resemble those of potassium and sodium that they are appropriately described in the same chapter. Following, therefore, are descriptions of the more important ammonium salts.

357. Ammonium Chloride, NH_4Cl.—This salt, known commercially as sal ammoniac, is formed when hydrochloric acid and ammonia gases are brought into contact. It is now manufactured by neutralising ammoniacal gas liquor with hydrochloric acid, evaporating the liquid and removing the crystals of the chloride. These are dried and gently roasted, in order to expel tarry matters. The crude chloride is then placed in an iron pan fitted with an iron cover, and sublimed: the chloride condenses on the lid and is thus obtained in tough and fibrous masses, which are remarkably difficult to powder.

The salt is also obtained by sublimation on heating together sodium chloride and ammonium sulphate:—

$$\underset{\text{Sodium}}{2NaCl} + \underset{\text{Ammonium sulphate.}}{Am_2SO_4} = \underset{\text{Ammonium chloride.}}{2AmCl} + \underset{\text{Sodium sulphate.}}{Na_2SO_4}.$$

The same plant is employed as that used for the purification of the chloride by sublimation.

Ammonium chloride is obtained in fine crystals by dissolving in boiling water and then stirring continually as the liquid cools. The salt crystallises in cubes and octahedra. Ammonium chloride sublimes without undergoing fusion, and has an abnormal vapour-density due to dissociation. It is used for cleansing the surfaces of metals about to be tinned or soldered, and also in dyeing.

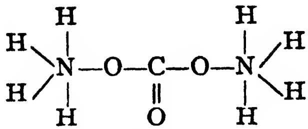
358. **Ammonium Sulphate, Am_2SO_4.**—Like the other compounds of ammonium, this body is prepared by neutralising ammoniacal gas liquor. In practice this is best performed by heating the liquor with lime and conducting the evolved gas into sulphuric acid until it no longer has an acid reaction to litmus. During this time continuous crops of crystals of ammonium sulphate are formed and removed. This body is soluble in water; melts when heated, and undergoes partial decomposition. At higher temperatures it is entirely decomposed. Ammonium sulphate is employed for manuring purposes.

359. **Ammonium Nitrate, Am_2NO_3.**—On dissolving ammonium carbonate in dilute nitric acid and evaporating, long prismatic crystals of this salt are obtained. They are deliquescent, melt on being heated, and are decomposed into nitrous oxide and water. The principal use of ammonium nitrate is in the manufacture of this gas.

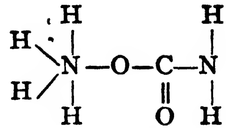
360. **Ammonium Carbamate.**—On mixing together dry ammonia gas and carbon dioxide, a substance is formed to which the name of ammonium carbamate has been given :—

$$\underset{\text{Ammonia}}{2NH_3} + \underset{\text{Carbon dioxide.}}{CO_2} = \underset{\text{Ammonium carbamate.}}{NH_4CO_2NH_2}.$$

This body has a somewhat anomalous composition; probably one of the NH_4O groups of the normal carbonate is replaced by NH_2, as indicated in the following graphic formulæ :—



Normal Carbonate.



Carbamate.

Combinations of anhydrous acids with dry ammonia cannot possibly yield normal salts, because ammonia is not a base: the compounds produced are minus the elements of water; thus with sulphuric anhydride, ammonium sulphamate, $(NH_3)_2SO_3$, is formed, a body the constitutional formula of which is probably $NH_4SO_3NH_2$. These bodies, termed -amates, are changed by the assimilation of water into normal salts :—

$$\underset{\text{Ammonium sulphamate.}}{NH_4SO_3NH_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4}.$$

So, too, in the presence of water, the carbamate undergoes the following change :—

$$\underset{\text{Ammonium carbamate.}}{NH_4CO_2NH_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Ammonium carbonate.}}{(NH_4)_2CO_3}.$$

In this way ammonium carbonate is obtained in solutions from which, if sufficiently concentrated, crystals are deposited on standing.

Commercial ammonium carbonate is manufactured by heating together a mixture of powdered chalk with half its weight of either ammonium chloride or sulphate; the carbonate sublimes and is condensed in leaden receivers. As thus produced the commercial product is a white translucent fibrous mass, with a powerful ammoniacal smell. The salt thus obtained is a mixture of the carbamate with hydric ammonium carbonate, and may be represented by the formula $NH_4CO_2NH_2 + NH_4HCO_3$. On exposure to the air this salt gradually evolves ammonia by the decomposition of the carbamate :—

$$\underset{\text{Ammonium carbamate.}}{NH_4CO_2NH_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Hydric ammonium carbonate.}}{NH_4HCO_3}.$$

For laboratory purposes, the commercial salt is dissolved in

water and a little free ammonia added; in this way both carbamate and the hydric salt are transformed into the normal carbonate. On being heated, the commercial carbonate is readily decomposed into carbon dioxide and ammonia gases.

The hydric carbonate, NH_4HCO_3, is formed by the action of air on the commercial salt, and also by passing carbon dioxide to saturation through its solution, when crystals are deposited. This salt does not smell of ammonia, and is more stable than the normal carbonate.

361. Ammonium Sulphides.—Like potassium, ammonium forms several sulphides. Of these, the hydrosulphide, NH_4HS, is the most important; it is prepared by passing sulphuretted hydrogen to saturation into a solution of ammonia. To prepare the normal sulphide, the ammonia is divided into two equal parts, and only the one moiety saturated, after which the two are mixed together. Ammonium sulphide possesses an unpleasant odour, somewhat resembling that of sewer gas. By digesting sulphur in a solution of this compound, the disulphide and higher sulphides are formed.

Several sulphides, among which are those of arsenic and antimony, are soluble in the sulphide of ammonium; under these circumstances soluble sulpho-salts are formed, in which sulphur replaces the oxygen. Thus ammonium arsenite is Am_3AsO_3, while the sulpharsenite is represented by Am_3AsS_3.

362. Other Ammonium Salts.—With most other acids ammonium forms salts which are analogous to those of potassium and sodium. The phosphates correspond with those of sodium; as a blowpipe reagent, that known as microcosmic salt is sometimes employed. It is an acid double salt of ammonium and sodium, represented by the formula $NaNH_4HPO_4,4H_2O$. This fuses into sodium metaphosphate, and as such acts as a solvent for various oxides in blowpipe analysis.

Ammonia combines with many salts in somewhat the same way as does water of crystallisation, forming compounds termed ammoniated salts; of these ammoniated silver chloride, $AgCl,2NH_3$ is one of the best known examples.

A number of substitution salts of ammonium are also known in which part of the hydrogen is replaced by other elements or compounds. Among these may be instanced mercury 'white precipitate,' a body represented by the formula NH_2HgCl. This body may be viewed as ammonium chloride with two atoms of hydrogen replaced by one of dyad mercury.

CHAPTER XXIII

METALS OF THE ALKALINE EARTHS

Calcium.—Symbol, Ca. Atomic weight, 39·9.

363. **Occurrence.**—This element is never found in the free state in nature; but, in combination with other elements, is one of the most plentiful and widely distributed elements in the earth's crust. It is a constituent of igneous rocks, and in the form of carbonate constitutes by far the greater portion of stratified rock-formations.

364. **Preparation and Properties.**—The metal is only obtained in the free state with difficulty. It may be procured by the electrolysis of fused calcium chloride, or by heating calcium iodide in a closed crucible, under pressure, with metallic sodium. The metal is yellowish in colour, may be kept for some time in dry air, but oxidises at once on being thrown into water, with the separation of hydrogen and formation of calcium hydrate. On being heated in air the metal burns, but in a closed vessel, free from oxygen, may be raised above the boiling-point of zinc without undergoing volatilisation. It is only in combination that this metal possesses great importance.

365. **Calcium Chloride, $CaCl_2,6H_2O$.**—In many chemical reactions, including those of the manufacture of ammonium carbonate, and of sodium carbonate by the ammonia process, calcium chloride is obtained as a bye-product. It may also be readily prepared by dissolving chalk or marble in hydro-

chloric acid. On evaporating the solution colourless crystals of the salt are obtained; these are very soluble in water, and extremely deliquescent. On being gently heated, the crystals evolve a portion of their water, and form a porous substance, having the formula, $CaCl_2,2H_2O$. In this form the so-called fused calcium chloride is a most energetic absorbent of water. It is in consequence of great value in the laboratory as a drying agent. At higher temperatures the chloride fuses and becomes anhydrous; at the same time a portion of the salt is decomposed with the evolution of a little hydrochloric acid, and consequent formation of calcium oxide (lime). This fused mass presents less surface, and so does not act so well as a desiccating agent as the form prepared at a lower temperature.

366. **Calcium Fluoride, CaF_2.**—This, under the name of fluor-spar, is one of the best known minerals, as it occurs—especially in Derbyshire—in cubical and octahedral crystals of great beauty. The mineral is either colourless, or of various pink, green, or blue tints, due to traces of impurities. Calcium fluoride is insoluble in water, but is slightly attacked by hydrochloric acid, and also on being heated with chlorine. Concentrated sulphuric acid transforms it into calcium sulphate, with the escape of hydrofluoric acid as described in connection with fluorine. On being gently heated, some kinds of fluor-spar, especially a massive variety termed chlorophane, become faintly luminous, with a greenish light, long before they approach a red heat. This property, which is also possessed by other substances, has received the name of fluorescence. On being more strongly heated, fluor-spar melts, doing this much more readily when mixed with the siliceous matters of metallic ores, which thus form a fusible slag. From the property of acting as a flux, this body has been named *fluor* spar, from the Latin *fluo*, I flow.

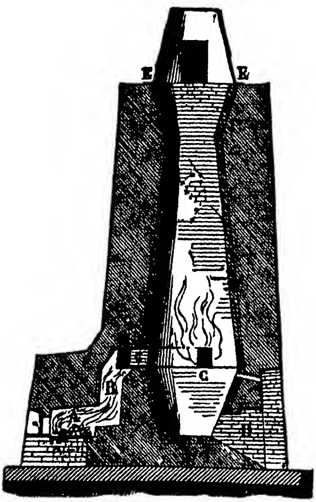
367. **Calcium Oxide, CaO.**—This body, under the name of lime, has been known from almost the earliest ages. Lime does not occur in the free state in nature, but may readily be manufactured from limestone.

Preparation.—In the pure state, lime may easily be pre-

pared by heating calcium nitrate to redness; nitrous fumes are evolved, and lime remains behind as a porous mass. On heating black marble (calcium carbonate) for one or two hours to a full red heat, almost pure lime is also obtained.

Manufacture.—On the large scale enormous quantities of lime are 'burnt' in specially constructed furnaces, called kilns. These are constructed so as to be used either intermittently or continuously; in the former case a charge of limestone (natural carbonate) is introduced; fuel is placed underneath and allowed to burn. When the operation is complete the lime is removed, and another charge inserted in the furnace. The continuous kilns are operated on another principle; a kiln of this kind is shown in figure 70. The total height of the kiln may be about 20 feet, and the diameter some 5 feet. At the bottom A is the fireplace, with flue, B, branching off into C and C′, and entering the interior of the kiln around its sides. The kiln is fed with limestone from the top, which gradually descends as from time to time the completely burned lime is removed through D. Limestone that is slightly damp loses its carbon dioxide more readily than when perfectly dry; so, too, the burning takes place more readily in damp than in dry weather. It is probable that the steam in the kiln assists the decomposition owing to its forming a hydrate which is as quickly decomposed. The heat must not be allowed to rise too high during lime-burning, as if so the lime is injured by the silica present in the stone fusing, and forming an insoluble coating over the pieces.

FIG. 70.



Properties.—Burned lime, or quicklime as it is frequently termed, is a white solid, and is one of the most infusible sub-

stances known, being employed in the preparation of crucible and furnace linings where the highest attainable temperatures are employed. Lime combines wirh water, with the evolution of great heat, and the formation of calcium hydrate, $Ca(HO)_2$.

The lime obtained from pure limestones is termed rich or fat lime; those from impure limestones, containing magnesia and clayey matters, are termed poor or meagre limes.

Industrial Applications.—The greater number of purposes for which lime is employed require its first being converted into the hydrate, under which head they will be described.

368. Calcium Hydrate, $Ca(HO)_2$.—By the combination of quicklime with water, this compound, known also as slaked or 'slack' lime, is produced.

Preparation.—When lime is treated with water in the proportion of a molecule of each (about 3 parts of lime to 1 of water), the hydrate is formed:—

$$\underset{\text{Calcium oxide.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Calcium hydrate.}}{Ca(HO)_2}.$$

Under these circumstances the resultant hydrate is a dry powder, and its production is accompanied by considerable elevation of temperature. For most purposes for which the hydrate is required, it is mixed with water in much larger quantity; it then breaks down into a smooth, creamy paste. This, when further diluted with water, forms the 'milk of lime' directed to be used in many experiments and manufacturing operations.

Properties.—Calcium hydrate is a white powder, one part of which is soluble in 780 parts of cold water, and in about half that quantity of boiling water. The solution thus prepared is that known as lime-water; it has an alkaline disagreeable taste, and turns reddened litmus solution blue. Slaked lime, whether in the form of the dry powder, a paste, or in solution, combines readily with carbon dioxide, forming the insoluble carbonate.

Industrial Applications.—The principal and most important use to which lime is applied is in the preparation of mortars and cements. In addition, lime is used in the manu-

facture of glass, bleaching powder, caustic alkalies and ammonia, and many other substances.

Lime is also employed when mixed with water as lime-wash; in this form it not only whitens rooms or buildings whose walls are thus treated, but also acts as a valuable antiseptic and disinfectant. Lime is also used as a manure.

There are many other uses of lime too numerous to mention in detail.

369. Mortars and Cements.—Mortar essentially consists of one part of lime slaked into a paste, and mixed with three to four parts of fine sand, that of a sharp and angular nature being preferred. In building, the joints between the bricks or stones are filled with this material, each brick being pressed down in its place on a bed of mortar The mortar first dries by the evaporation of its moisture, and then gradually hardens or 'sets,' as a result of the absorption of atmospheric carbon dioxide. This change is, however, only superficial, for in the centre of set mortar, even that which is centuries old, lime is still found in the uncombined condition.

Certain limestones which contain some 30 per cent. of clayey matter produce a mortar which hardens under water. Such limestones require to be burned very carefully, so as to just set free alumina from the clay, calcium silicate also being formed. The lime thus produced is termed 'cement,' of which one well-known variety is Roman cement. These cements harden as the result of the formation of a compound of lime with alumina on their being wetted.

370. Calcium Sulphate, $CaSO_4$.— This substance occurs native and is known as *anhydrite*; a much more usual variety of the sulphate is that termed gypsum, which crystallises in prisms and contains two molecules of water of crystallisation. The sulphate may be prepared by the action of sulphuric acid on the carbonate, but the native compound serves for practically all purposes to which this salt is applied.

Properties.—Calcium sulphate is slightly soluble in water, which at about 15° C. dissolves about 1 part in 500 of the salt. Most spring waters contain calcium sulphate as an impurity,

and to this owe their permanent hardness. On gently heating gypsum, the mineral loses its two molecules of water, and yields a dry, white powder consisting of the anhydrous substance; this powder possesses the remarkable property of being able to again combine with the two molecules of water, and in so doing forms a solid substance. Gypsum thus dried and ground constitutes the body well known as 'plaster of Paris.' If the plaster be made into a thin paste, and poured into a mould of any desired shape or form, it becomes solid in a few moments, and thus affords a very perfect reverse impression of the mould.

Industrial Applications.—In addition to its extensive employment as plaster of Paris, gypsum is used as a manure.

371. **Calcium Carbonate, $CaCO_3$.**—Enormous quantities of this mineral occur in nature in a more or less pure form. Large transparent crystals occur, to which the name of Iceland spar is given; these are almost chemically pure calcium carbonate. The white crystalline marbles of Carrara are also very pure. Larger masses of stratified limestones contain, as impurities, clay and other substances.

Preparation.—In the chemically pure form, calcium carbonate may be obtained by precipitating calcium chloride with ammonium carbonate, and carefully washing and drying.

Properties.—This salt is insoluble in pure water, but dissolves in water containing carbonic acid in solution. It thus forms an acid carbonate, to which is due the temporary hardness of waters. On being heated, the carbonate decomposes with the production of the oxide, CaO, and escape of carbon dioxide. Two distinct crystalline shapes of this mineral are known, which is therefore dimorphous.

Industrial Applications.—The great use of calcium carbonate is in the manufacture of lime and cements. In addition, the limestones form a most important class of building materials.

372. **Calcium Phosphate, $Ca_3(PO_4)_2$.**—This phosphate occurs native as a mineral, and also is the principal constituent of bone-ash. The phosphate is insoluble in water, but by the action of sulphuric acid may be converted into the acid- or

superphosphate, $H_4Ca(PO_4)_2$. In this form it is soluble, and is largely used as a manure.

373. **Other Salts of Calcium.**—Calcium nitrate, $Ca(NO_3)_2$, is a very deliquescent body formed when the carbonate is dissolved in nitric acid. Calcium forms sulphides, which are soluble in water. By heating pure lime with sulphur in the dry way a sulphide is obtained, which after exposure to strong light, becomes luminous, and remains so for a considerable time. In this condition it forms the basis of what are termed luminous paints.

Barium.—Symbol, Ba. Atomic weight, 136·8.

374. **Occurrence.**—Barium does not naturally occur in the free state, but is known as the sulphate in baryta or heavy spar, so called because of its high specific gravity.

375. **Preparation and Properties.**—Metallic barium may be prepared by the electrolysis of barium chloride in the presence of mercury, when an amalgam of barium is formed; on heating, the mercury is volatilised and metallic barium remains. The metal quickly tarnishes and decomposes water at ordinary temperatures with the escape of hydrogen gas.

376. **Barium Chloride, $BaCl_2$, $2H_2O$.**—This salt may readily be prepared by dissolving the native carbonate in hydrochloric acid. On the large scale it is manufactured by fusing together calcium chloride and barium sulphate, when double decomposition occurs. The fused mass is rapidly extracted with hot water, when the difficultly soluble calcium sulphate remains behind. On crystallisation the salt is obtained in rhombic tables which contain two molecules of water. Barium chloride is a soluble non-deliquescent salt, largely used in the laboratory, and also on the manufacturing scale for the precipitation of insoluble barium sulphate.

377. **Barium Oxide, BaO.**—This substance is most readily obtained by heating the nitrate to redness, when the oxide remains as a greyish-white substance. Barium oxide may be fused by the heat of the oxyhydrogen blowpipe. The

oxide combines readily both with water and with carbon dioxide.

Barium Peroxide, BaO_2.—On being heated to a dull red heat, barium oxide combines with another atom of oxygen, forming the peroxide, BaO_2. This body is soluble in water, from which it crystallises in plates, having the composition, $BaO_2,8H_2O$. Barium peroxide loses its extra atom of oxygen on being heated to a still higher temperature than that required for its first production; or the same change may be induced by lowering the atmospheric pressure, with the temperature remaining constant. The Brin oxygen manufacturing process is based on this reaction. Barium peroxide is also used in the preparation of hydrogen peroxide.

378. Barium Hydrate, $Ba(HO)_2$.—On slaking the oxide, BaO, with water, this compound is formed. It is soluble in three parts of boiling and twenty parts of cold water, thus producing a strongly alkaline liquid, from which a crystalline hydrate of the composition, $Ba(HO_2),8H_2O$ may be obtained. The hydrate fuses at a low red heat, but retains its water at still higher temperatures. Barium hydrate forms the insoluble carbonate $BaCO_3$, when exposed to carbon dioxide, behaving in this way very similarly to lime-water, instead of which substance it is frequently employed in the laboratory as a carbon dioxide absorbent. The solution of barium oxide is now largely used in sugar-refining instead of lime. On the large scale the oxide is prepared by passing superheated steam over the heated carbonate.

$$\underset{\text{Barium carbonate.}}{BaCO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Barium hydrate.}}{Ba(HO)_2} + \underset{\text{Carbon dioxide.}}{CO_2}.$$

379. Barium Sulphate, $BaSO_4$.—This is the most important natural compound of barium; it is distinguished by its high specific gravity, 4·59, and consequently has received its name of heavy spar. Barium sulphate is almost absolutely insoluble in water, and only very slightly soluble in dilute acids. The sulphate is readily obtained by precipitation of any solut salt of barium with sulphuric acid, or a sulphate. This ı

serves for the quantitative estimation of both barium and sulphuric acid. On being heated with charcoal, barium sulphate is reduced to sulphide ; and by this reaction many of the soluble salts of barium are obtained. Barium sulphate is used as a white pigment, and as an adulterant of white lead.

380. Barium Sulphide, BaS.—The mono-sulphide, BaS, is obtained by the reduction of the sulphate by heating with starch, flour, or other convenient source of carbon. The mass is lixiviated with hot water, and a solution obtained, from which crystals, having the composition $BaS,6H_2O$, are deposited. This salt is employed as the source of other barium compounds.

381. Barium Carbonate, $BaCO_3$.—This body occurs native as the mineral, witherite, and may readily be prepared artificially by the precipitation of barium chloride or nitrate with a soluble carbonate. Barium carbonate is insoluble in water, and does not, when dry, lose its carbon dioxide at even very high temperatures. The heated carbonate is, however, decomposed by the action of a current of superheated steam.

382. Other Salts of Barium.—Among these the nitrate $Ba(NO_3)_2$, is practically the only one requiring mention. It is readily prepared by dissolving the carbonate in nitric acid and crystallising out the salt. Barium nitrate is employed in the manufacture of 'green fire' and other fireworks. It is also employed in the laboratory as a substitute for the chlorides in those reactions in which the presence of a chloride is inadmissible.

Barium chlorate, $Ba(ClO_3)_2$, is a convenient source ot chloric acid, because of the readiness with which the barium may be removed by cautious addition of sulphuric acid. Owing to this property, barium salts of various acids are first prepared, as a source of the acids themselves.

Strontium.—Symbol, Sr. Atomic weight, 87·2.

383. Occurrence.—This element is much less plentiful than barium; its natural sources are the sulphate, celestine, and the carbonate, strontianite. By processes similar to those

employed for the preparation of barium, metallic strontium is obtained. Both the metal and its salts bear a close resemblance in character to those of barium.

384. **Strontium Chloride, $SrCl_2,6H_2O$.**—This salt may be obtained by dissolving the native carbonate in hydrochloric acid and subjecting the liquid to crystallisation. The salt is deliquescent, and soluble in water. Its solution in alcohol burns with a most intense crimson flame.

385. **Strontium Oxide, SrO.**—This body may be obtained from the nitrate by ignition. It slakes on being mixed with water, and forms a crystalline hydrate of the composition $Sr(HO_2),8H_2O$. This in solution readily absorbs carbon dioxide, with the formation of the carbonate. A peroxide, SrO_2, is also known.

386. **Strontium Sulphate, $SrSO_4$.**—This salt occurs native, but, while resembling the sulphate of barium in crystalline form, is distinguished by its lower specific gravity, 3·9. Strontium sulphate is feebly soluble in water, about one part in 7,000; it is, however, much more soluble in dilute acids and solutions of sodium chloride and other salts.

387. **Strontium Carbonate, $SrCO_3$.**—This salt is insoluble in water, but soluble in dilute acids. It is readily prepared by precipitating a soluble strontium salt with ammonium carbonate. Strontium carbonate is not decomposed by heat alone into the oxide and carbon dioxide.

388. **Strontium Nitrate, $SrNO_3$.**—By dissolving the carbonate in dilute nitric acid, and evaporating, the nitrate is obtained as colourless crystals. The salt is soluble in water. Mixed in the dry state with sulphur and various ordinary agents, it forms the mixture known as 'red fire.' On being heated the nitrate is resolved into the oxide, with evolution of nitrogen oxides and oxygen.

CHAPTER XXIV

THE ZINC GROUP

Magnesium.—Symbol, Mg. Atomic weight, 23·94.

389. Occurrence.—In a state of combination, magnesium is a widely distributed element. It occurs in certain igneous rocks, also in dolomite, or magnesian limestone, a double carbonate of calcium and magnesium. The sulphate occurs in the water of many mineral springs, and the chloride in sea-water.

390. Extraction.—Magnesium is obtained on a fairly large scale by the reduction of its chloride by metallic sodium. The magnesium chloride is mixed with about one-sixth of its weight of each of sodium chloride and calcium fluoride, which latter acts as a flux. A sixth part of sodium in small pieces is added, and the whole raised to a bright-red heat in a covered clay crucible. The reducing action being over, the mixture is stirred, in order to get the metal to run into a button: it is then poured, and after solidification, extracted from the slag. As the metal thus prepared contains carbon and other impurities, it is now usually distilled in a covered crucible, fitted with an iron tube passing up through a hole in the bottom to just above the surface of the melted metal. On being subjected to a strong heat, the metal volatilises, and its vapour being very heavy, passes readily downward through the iron tube, condenses, and collects in a vessel arranged for its reception. This operation is often termed 'distillation *per descensum*.'

391. Properties.—Magnesium is a white metal, to which a high polish may be imparted. In an atmosphere of hydrogen this bright surface lasts indefinitely. In dry air a superficial film of oxide forms, while in the presence of moisture, the metal is gradually converted into oxide. Magnesium wire is prepared by forcing the metal, softened by heat, through an aperture in the cover of a press, within which the metal is

confined. This wire is converted into ribbon by being passed between a pair of rolls.

Magnesium readily takes fire on being heated in air, and burns with a dazzling bluish-white flame, forming the oxide, MgO. Both in the form of wire and powder, magnesium is being largely used as a source of artificial light for photographic purposes. Magnesium causes a slow evolution of hydrogen from water at boiling temperatures, and readily effects the decomposition of hydrochloric and sulphuric acids in the very dilute state, pure hydrogen being evolved.

392. **Industrial Applications.**—The principal uses to which magnesium is applied are those of obtaining a brilliant light either for photography, or signalling and other pyrotechnic purposes.

393. **Magnesium Chloride, $MgCl_2$.**—On sufficiently concentrating sea-water (and also that of some mineral springs), to remove most of the common salt, the 'bittern,' or bitter mother-liquor remaining, contains in solution both magnesium chloride and bromide. This solution yields on cooling, crystals having the composition $MgCl_2, 6H_2O$. Magnesium chloride is a deliquescent salt, very soluble in water. On being heated, this salt is decomposed, with evolution of hydrochloric acid and water, leaving behind a residue of magnesia, MgO. If the salt be first mixed with ammonium chloride, prior to ignition, and then carefully raised to a red heat, it fuses to a clear liquid, which acquires a crystalline structure on cooling. This body is the salt in its anhydrous form. Magnesium chloride is employed in the preparation of cotton goods.

394. **Magnesium Oxide, MgO.**—This body, called also magnesia, is obtained as a white pulverulent substance, when magnesium is burned in either air or oxygen. Other processes for its preparation consist in strongly igniting either the carbonate or nitrate. Magnesium oxide is a white powder, which is almost insoluble in water, but, nevertheless, when moistened shows a distinctly alkaline reaction to litmus and turmeric papers. In the oxyhydrogen flame, magnesia is fused to a porcelain-

like substance. Magnesia slowly combines with water to form a hydrate, $Mg(HO)_2$; the same compound is produced on adding potassium hydrate to a solution of a magnesium salt. The hydrate slowly absorbs and combines with atmospheric carbon dioxide.

395. Magnesium Sulphate, $MgSO_4,7H_2O$.—This salt is found in nature, combined with seven molecules of water as shown above, and also in combination with one molecule, in which form it is known as kieserite. The former modification, called Epsom salts, is very soluble in water, while the latter is as insoluble as gypsum. Not only may the sulphate be obtained from these sources, but it is also formed by dissolving the carbonate in sulphuric acid. Formerly, large quantities of the Epsom salts of commerce were thus obtained, but at present most is derived either from the natural sulphate beds of Stassfurt or from sea-water bittern. The ordinary magnesium sulphate is soluble in about three parts of water, and forms a solution having a bitter taste. Epsom salts are largely used in medicine. On heating the crystallised sulphate it readily loses six of its molecules of water of crystallisation, thus forming the modification named kieserite, $MgSO_4,H_2O$. The molecule of water in kieserite may be replaced by the molecule of an alkaline sulphate, as that of potassium, thus $MgSO_4,K_2SO_4,6H_2O$. This double salt of magnesium and potassium crystallises with six atoms of water and is isomorphous with the ordinary sulphate.

396. Magnesium Carbonate, $MgCO_3$.—The normal carbonate occurs in nature as the mineral magnesite. It may be prepared by the precipitation of magnesium chloride with either potassium or sodium carbonate, and then dissolving the precipitate into carbonic acid water. With the escape of the acid, crystals, having the composition $MgCO_3,3H_2O$, are deposited.

The precipitate caused by adding sodium carbonate to magnesium sulphate consists of a mixture of the carbonate and hydrate of magnesium in varying proportions; this body is

known commercially as magnesia alba. Magnesium carbonate is readily soluble in water containing ammonium chloride.

397. **Magnesium Silicates.**—These constitute an important class of minerals; among them are the following:—

Talc	$(MgO)_4(SiO_2)_5$.
Steatite . . .	$(MgO)_3(SiO_2)_4$.
Meerschaum . .	$(MgO)_2(SiO_2)_3(H_2O)_4$.

In addition to these a great number of double silicates of magnesium and other metals are known.

398. **Other Salts of Magnesium.**—Among these may be mentioned the phosphates, one of which is employed as the means of separating magnesium for the purpose of determining it quantitatively. On adding a mixture of sodium phosphate and ammonium chloride to a solution of a magnesium salt, ammonic magnesium phosphate, $MgAmPO_4$, is precipitated as a fine crystalline precipitate. On ignition, this is changed into the pyrophosphate, $Mg_2P_2O_7$.

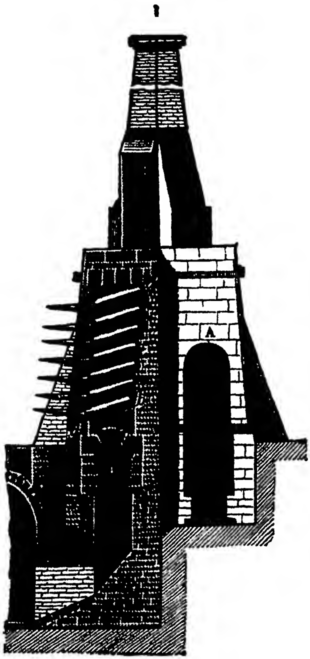
Zinc.—Symbol, Zn. Atomic weight, 64·9. Melting-point, 412°. Boiling-point, 1040°. Density, 32·45. Molecular weight, 64·9.

399. **Occurrence.**—Zinc is one of those metals whose ores are fairly abundant. Principal among these are the sulphide, ZnS, known as zinc blende, the oxide, ZnO, known as red zinc ore, and calamine, which is a carbonate of zinc.

400. **Extraction.**—In order to extract zinc from its ores, these are first roasted, in order to convert them into oxides, if not already in that condition. The ore is next mixed with carbon and reduced by heat; at the same time the metal, owing to its volatility at high temperatures, distils over and is collected in properly arranged receivers. The plant now most commonly used in this country is that known as the Belgian furnace, which is shown in fig. 71. The mixed ore and charcoal or coal is placed in the cylindrical retorts, *a b*, which are each about 8 inches diameter and 3 feet in length. They are closed at one end, and are arranged in tiers in the furnace, with their open

ends pointing downwards, as shown at *a b c d.* To the mouth of each retort a conical tube about 10 inches long is fixed. The furnace is first brought to a high temperature, and then the filled cylinders inserted; as they become hot, the zinc is reduced and carbon monoxide emerges and burns at the mouth of each retort. After a while the flame assumes a greenish-white appearance, which is a sign that zinc has commenced to distil over. The greater part of the zinc condenses in the cast-iron cover attached to the mouth of each cylinder. Periodically, these have the melted zinc raked out by the workman in charge; in twelve hours the whole operation is complete, and the one cylinder is replaced by another freshly filled with the mixture of ore and carbon. The zinc is skimmed and cast into ingots. For its further purification, zinc may be redistilled.

FIG. 71.



401. Properties.—Zinc is a bluish-white metal, showing a brilliant crystalline surface on being fractured. The outside of the metal rapidly acquires a coating of oxide which, being adherent, protects the interior. At ordinary temperatures zinc is too brittle to be rolled or otherwise worked, but at a temperature of 100°–125° zinc becomes so malleable that it may readily be rolled into sheets. At higher temperatures, 200°–210°, the metal becomes so brittle that it may be pounded to a fine powder in a mortar. Zinc at the boiling-point burns with a brilliant white light, with the production of zinc oxide, ZnO. The vapour of zinc has a density which is half the atomic

weight; therefore the molecule of zinc vapour must contain but one atom of the metal. Zinc decomposes water at high temperatures; in the pure state it is scarcely at all affected by dilute hydrochloric or sulphuric acids, but in the commercial form readily attacks these acids with abundant evolution of hydrogen.

402. Industrial Applications.—Zinc is employed for the purpose of coating iron vessels, which are first rendered chemically clean and then dipped into melting zinc. Such vessels are said to be galvanised. In the form of sheeting, zinc is used for roofing and other purposes.

In combination with other metals zinc forms brass and other valuable alloys; for descriptions of these, and also other departments of metallurgy proper, the student is referred to Bloxam and Huntington's text-book on *The Metals.*

403. Zinc Chloride, $ZnCl_2$.—Zinc combines directly with chlorine to form this chloride; it is more usually, however, prepared by dissolving zinc in hydrochloric acid, and concentrating the solution by evaporation, when the temperature rises until it arrives at 250°, when the chloride becomes anhydrous. Zinc chloride is a white, very deliquescent body, which possesses powerful caustic properties. At a red heat, it distils, yielding a vapour which has the density 66·38; this figure agrees closely with the number 67·8, required by the formula $ZnCl_2$. Zinc chloride is a powerful antiseptic, and its solution has been introduced for disinfecting purposes under the name of Burnett's Disinfecting Fluid.

404. Zinc Oxide, ZnO.—Red zinc ore is an impure native oxide; in the pure state this compound is white. It is prepared on the large scale by distilling zinc into chambers in which it meets a current of air; the metal burns and deposits flakes of the oxide. This is treated with water, when the metallic zinc present sinks readily to the bottom, and is so separated. The oxide becomes yellow when heated, and recovers its white colour on cooling. The hydrate $Zn(HO)_2$ is formed on the addition of sodium or potassium hydrate to a soluble salt of zinc.

Zinc oxide is used as a substitute for white lead in the preparation of oil paints; although a much more permanent white, it has the defect of possessing very little of what painters call *body*, and so does not cover well.

405. Zinc Sulphide, ZnS.—The native sulphide, zinc blende, usually contains also large quantities of iron sulphide, and so is frequently almost black. The precipitated sulphide is white in colour, and may readily be obtained by adding ammonium sulphide to a solution of zinc sulphate. The artificial sulphide is readily dissolved by acids, with evolution of sulphuretted hydrogen; but the mineral form is not so readily attacked. On being roasted in air zinc sulphide is converted into the oxide.

406. Zinc Sulphate, $ZnSO_4,7H_2O$.—If zinc sulphide be roasted in air at temperatures below those at which it is converted into oxide, the sulphide is partly oxidised into sulphate, and may thus be obtained by lixiviation and subsequent crystallisation. More frequently, however, zinc sulphate is prepared by the action of dilute sulphuric acid on metallic zinc. It is obtained in colourless prismatic crystals, and is very soluble in water. Like magnesium sulphate it forms double salts, which crystallise with six molecules of water. Zinc sulphate is used in medicine, and also as a mordant in dyeing and calico-printing.

407. Zinc Carbonate, $ZnCO_3$.—This is the earliest known of the ores of zinc; in the native state it forms the mineral known as calamine. It readily loses carbon dioxide on being heated. On adding normal sodium or potassium carbonate to a solution of zinc salt a basic carbonate is precipitated in which the proportion of base varies. The following is the formula of one of these carbonates:—$(ZnO)_8(CO_2)_3,6H_2O$. If the acid potassium carbonate be added in excess, normal zinc carbonate is precipitated in the hydrate form.

408. Other Salts of Zinc.—Among other compounds of zinc is zinc silicate, known when native as electric calamine, and having the formula $(ZnO)_2SiO_2H_2O$. Zinc bromide and

iodide resemble the chloride in properties. Zinc nitrate is a colourless deliquescent salt.

Cadmium.—Symbol, Cd. Atomic weight, 111·6. Melting-point, 227·8. Boiling-point, 860°. Density, 55·8. Molecular weight, 111·6.

409. **Occurrence and Extraction.**—When distilling some varieties of zinc ore, prior to the appearance of the characteristic zinc flame at the mouths of the retorts, there is a brownish-coloured flame, known by the smelters as 'brown blaze.' The occurrence of this is due to the presence of cadmium in the ore; and as that metal has a lower boiling-point than zinc, it distils over first. This portion of the distillate is kept separate, dissolved in sulphuric acid, and the cadmium precipitated as sulphide by sulphuretted hydrogen. The sulphide is dissolved in strong hydrochloric acid, precipitated as carbonate by ammonium carbonate, dried and reduced by heating with carbon, and then purified, if necessary, by distillation.

410. **Properties.**—Cadmium is a white soft metal, which, like zinc, forms a monatomic molecule. It melts and distils at a lower temperature than zinc; like that metal it is readily dissolved by dilute hydrochloric or sulphuric acids, with evolution of hydrogen.

411. **Cadmium Salts.**—The halogen salts bear a general resemblance to those of zinc; the chloride is represented by the formula $CdCl_2$, and crystallises with two molecules of water. The iodide, CdI_2 is used in photography.

Cadmium oxide, CdO, is formed when the metal burns in air, and is a brown powder. A white hydrate is precipitated by the action of sodium or potassium hydrates on the solution of a soluble salt. The sulphide, CdS, is of a brilliant yellow colour, and is valued because of its permanency as a pigment. Cadmium sulphate is obtained by dissolving cadmium, or the oxide, in dilute sulphuric acid: it crystallises from concentrated solutions as $(CdSO_4)_3,8H_2O$. The nitrates and other salts are not of special importance.

CHAPTER XXV

ALUMINIUM AND IRON GROUPS

Aluminium.—Symbol, Al. Atomic weight, 27·3.

412. Occurrence.—This metal does not exist in the free state in nature, but, in combination with oxygen and silicon, is the essential metallic constituent of clays, slates, and argillaceous rocks generally, and also of the great majority of igneous rock-forming minerals.

413. Extraction.—Aluminium is one of the group of metals for whose manufacture on the large scale we are indebted to the powerful reducing action of metallic sodium. The most convenient aluminium compound to employ for this purpose is the mineral known as bauxite, which is a species of clay containing comparatively little silica. The mineral is finely ground and heated in a reverberatory furnace with soda ash, by which means sodium aluminate, $(Na_2O)_3Al_2O_3$, is formed. The cool, fused mass is extracted with water, and treated with sufficient hydrochloric acid to combine with the sodium; the aluminium then separates as the hydrate, $Al_2(HO)_6$. This is made into a paste with a mixture of common salt and charcoal, moulded into balls, and then thoroughly dried, after which the mixture is heated in cylinders through which dry chlorine is passed. Under this treatment a double chloride of sodium and aluminium, $(NaCl)_2Al_2Cl_6$, distils over and condenses in the solid form. This salt is mixed with sodium in the proportion of ten parts to two; five parts of cryolite, or fluor spar, are added to form a slag over the surface of the metal. The whole mixture is thrown on to the hot hearth of a reverberatory furnace, when a most violent reaction occurs between the sodium and the aluminium chloride, resulting in the following change:—

$$\underset{\text{Sodium aluminium chloride.}}{(NaCl)_2Al_2Cl_6} + \underset{\text{Sodium.}}{6Na} = \underset{\text{Sodium chloride.}}{8NaCl} + \underset{\text{Aluminium.}}{2Al.}$$

The melted aluminium collects beneath the slag.

414. Properties.—Aluminium is a white malleable metal, capable of taking a very high polish. It is distinguished by its very low specific gravity, 2·5, making it by far the lightest of the metals which are sufficiently stable to be employed for any practical purpose. Aluminium takes a very high polish, and does not tarnish in air, even when sulphuretted hydrogen is present. The metal is highly elastic and very sonorous in character, emitting a clear, bell-like sound on being struck. Intense heat in air only gives the metal a superficial coating of oxide, while a current of steam is only slowly decomposed by it at a full red heat. The metal burns in oxygen, with the production of alumina, Al_2O_3. Hydrochloric acid readily dissolves aluminium, with evolution of hydrogen and formation of aluminium chloride. Sulphuric acid also dissolves it, but more slowly. Nitric acid, whether dilute or concentrated, is without action on the metal at ordinary temperatures, but attacks it slowly on boiling. Hot solutions of potassium or sodium hydrates dissolve aluminium readily, with evolution of hydrogen and formation of aluminates of the metals.

415. Industrial Applications.—On the first manufacture of aluminium on the large scale great expectations were formed of this metal. Its great lightness and strength, together with its indifference to atmospheric corrosion, pointed to the possibility of important uses being made of the metal. The price, however, of aluminium has prevented its being extensively employed. For chemical balances, and other philosophical instruments, where lightness and strength are required, aluminium has been used. It forms with the metals some useful alloys, one of which, composed of aluminium and copper, is of a beautiful golden-yellow colour, and is somewhat extensively used in the manufacture of imitation jewellery.

416. Aluminium Chloride, Al_2Cl_6.—This body cannot be obtained in the anhydrous form by the 'wet' way, because, like many other chlorides, it is, during evaporation, decomposed, with an escape of hydrochloric acid and a residuum of alumina, Al_2O_3. In the dry way the chloride is prepared by heating small balls of a mixture of alumina and charcoal in

a current of dry chlorine, when the following reaction occurs:—

Al_2O_3	+	$3C$	+	$3Cl_2$	=	Al_2Cl_6	+	$3CO$.
Alumina.		Carbon.		Chlorine.		Aluminium chloride.		Carbon monoxide.

The chloride distils over, and condenses as a colourless translucent mass.

On exposure to air, aluminium chloride emits fumes of hydrochloric acid, undergoing slight decomposition. At a dull red heat the salt fuses, and then sublimes, forming a vapour having the density 134·19; this doubled gives the molecular weight as 268·38, that required by the formula Al_2Cl_6 being 266·8.

From an aqueous solution of the salt, evaporated at low temperatures, a chloride crystallises out, of the composition $Al_2Cl_6,12H_2O$.

417. Alumina, Al_2O_3.—This oxide occurs in nature in the crystalline form. When pure, the crystals are colourless, and then constitute the mineral termed corundum. At times crystals are found in which small quantities of other oxides are also present; these give definite and frequently very beautiful colours to the alumina. Thus the presence of chromium oxide imparts a red colour to the oxide of aluminium, which is then known as ruby. The sapphire also consists of alumina, coloured blue, most probably by small quantities of cobalt. Emery is an impure massive crystalline form of corundum.

Preparation.—By intense ignition of aluminium sulphate, the water and sulphuric acid are expelled, leaving behind a porous mass of aluminium oxide. It is exceedingly difficult, however, to drive off the last traces of acid. If an organic salt of aluminium be substituted, the alumina is more readily obtained, as such acids are decomposed with much greater readiness. Alumina may be prepared in the crystalline form by heating together in a furnace alumina and barium fluoride; a volatile fluoride of aluminium is formed, and this, in suffering decomposition, yields crystalline alumina. If a small quantity of potassium bichromate be added to the mixture, the crystals

have a rose-red colour, and are identical in appearance, constitution, and characters with the natural ruby.

Alumina is also formed on ignition of the hydrate, $Al_2(HO)_6$.

Properties.—The crystalline form of alumina is characterised by extreme hardness, being second only in this respect to the diamond. The natural crystals are insoluble in acids; but the artificial form, unless strongly ignited, dissolves, with the formation of salts.

Industrial Applications.—The hardness and extreme beauty of the natural ruby and sapphire have caused them to be much valued as gems. Smaller rubies are employed as bearings for the revolving spindles of watch-movements. The massive form, known as emery, is widely used as a grinding material for cutting down and polishing glass, steel, and iron-work, and other substances.

418. Aluminium Hydrate, $Al_2(HO_6)$.—The hydrated form of the oxide may be obtained by precipitating a soluble salt of aluminium by ammonia. It then occurs as a gelatinous semi-transparent precipitate, which can only be washed with difficulty. The precipitate dries into a horny mass, in which the composition is still $Al_2(HO)_6$. In this form alumina is readily dissolved by acids, or by strong bases, such as potash or soda. On being ignited, the hydrate shrinks, loses its water, and is converted into the oxide Al_2O_3.

Alumina is a weak base, but forms several well-known and important salts. Like several other metallic bases of weak character, it acts as an acid to very strong bases; hence its solution by the caustic alkalies, when aluminates are formed.

Industrial Applications.—The gelatinous nature of alumina leads to its receiving several very important applications as a clarifying and purifying agent. Thus, if it be added to sugar solutions, the alumina in subsiding carries down cloudy and other impurities, and leaves a clear supernatant solution. On the large scale it has been proposed to employ aluminium hydrate for the purpose of purification of effluent sewage-water. The impurities are to be carried down with the pre-

cipitated alumina, leaving behind a comparatively innocuous liquid. As a converse of this, certain pigments, called lakes, are prepared by precipitating aluminium hydrate in the coloured solutions, when the colouring matter is carried down by the precipitate. The most important use of aluminium hydrate is in dyeing, when it attaches itself in the manner described to the colour and also to the fibre of the material to be dyed. In this way the colour is bitten into the cloth, and cannot be removed by ordinary washing. Substances possessing this property are called mordants.

419. **Aluminates.**—Of these, the most important is sodium aluminate, $Na_6Al_2O_6$, the preparation of which from bauxite has been already described. The alkaline aluminates are formed in the wet way by the action of sodium or potassium hydrate solutions on precipitated alumina. Several mineral substances are aluminates; among these is the spinelle ruby, magnesium aluminate, $MgAl_2O_4$. Modifications of the spinelle are formed by the substitution of other metals in different proportions for the magnesium and aluminium of the primary aluminate.

420. **Aluminium Sulphate, $Al_2(SO_4)_3,18H_2O$.**—This body occurs in nature, and in the pure state may be prepared by dissolving the hydrate in sulphuric acid.

Manufacture.—Aluminium sulphate is manufactured on a somewhat extensive scale by roasting finely-powdered clay, or china clay, and then heating with sulphuric acid. The residual mass is extracted with water and thus separated from the silica of the clay, and also any undecomposed alumina. The solution is treated with potassium ferrocyanide to precipitate iron, and is then evaporated and the residue sold as concentrated alum or sulphate of alumina. The clays are aluminium silicates, usually contaminated with iron, but China clay, being an almost pure variety, yields a sulphate practically free from iron. An impure form of sulphate is introduced into the market under the name of alum-cake; this consists of the whole mass obtained on heating together China clay and sulphuric acid.

Properties.—Aluminium sulphate in its ordinary form is

very soluble in water, and has a strong acid reaction. It crystallises only with difficulty, and then forms thin plates belonging to the monoclinic system. Aluminium sulphate combines readily with other sulphates to produce double sulphates, which will be further described under the name of alums.

Industrial Applications.—Aluminium sulphate is used as a mordant, while crude alum-cake is largely employed for adding weight to paper.

421. Potash Alum, $K_2Al_2(SO_4)_4,24H_2O$.—Because of the difficulty in obtaining aluminium sulphate in the crystalline form, that salt is usually prepared as a double sulphate, either with potassium or ammonium. Both these bodies crystallise easily.

Manufacture.—Alum may be prepared by adding to crude aluminium sulphate solution the equivalent quantity of potassium sulphate, and then crystallising the salt.

A method more extensively employed is that of roasting and subsequently treating alum shale in the following manner. The alum shale is a bituminous clay, containing large quantities of iron pyrites (ferric sulphide). Some of the shale is sufficiently rich in bituminous matter to burn itself; other lots require to be mixed with coal. In either case the shale is made into heaps and roasted by being allowed to gently burn. During the roasting the ferric sulphide gives off sulphur, which is oxidised to sulphuric acid, and thus forms both aluminic and ferrous sulphates. It is then lixiviated, and the liquid heated with iron turnings, in order to reduce any ferric iron present to the ferrous state. As much as possible of ferrous sulphate is then removed by crystallisation. To this liquid either potassium sulphate or chloride is added; the latter being now more frequently used in the form of the crude Stassfurt salt. In this case sufficient ferrous sulphate should be present in the liquid to produce potassium sulphate by double decomposition.

$$\underset{\text{Potassium chloride.}}{2KCl} + \underset{\text{Iron sulphate.}}{FeSO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Iron chloride.}}{FeCl_2}.$$

The mixture is kept in a state of agitation, and alum sepa-

rates in small crystals. These are washed and dissolved in water and purified by re-crystallisation.

Properties.—Alum as thus prepared occurs in large octahedral crystals, which are readily soluble in hot and sparingly soluble in cold water. The solution has a drying, astringent taste, and is acid in reaction. Alum, on being heated, melts in its water of crystallisation, and then dries into a porous spongy mass known as burnt alum. Further ignition partly decomposes alum, with loss of sulphuric acid.

Ammonia Alum, $Am_2Al_2(SO_4)_4,24H_2O$.—If ammonium sulphate be substituted for that of potassium an alum is obtained which is almost exactly similar to ordinary or potash alum, except that it contains ammonium in place of potassium. In places where ammonium sulphate is cheaper, this form of alum is generally prepared, as for all ordinary purposes the two are equally serviceable. Prior to the discovery of the Stassfurt beds, it seemed probable that ammonium sulphate from gas liquor would almost entirely replace potassium salts in the production of alum. Ammonia alum, on being heated, leaves only aluminium sulphate, which, on intense ignition, is converted into alumina.

Industrial Applications.—The most important of these with alum is as a mordant in dyeing. The solution of alum is treated with sodium carbonate so long as the precipitate thus formed is re-dissolved. The liquid is then neutral to test-paper and readily parts with its alumina to cloth dipped in it. The alumina adheres most strongly both to the fibre of the cloth and also the colouring matter, and so effects their permanent combination. Alum is also used in sizing paper, and in effecting the deposition of muddy matters from sewage-water, towards which it also acts as a disinfectant.

422. Constitution of the 'Alums.'—It will have been observed that in constitution both the potash and the ammonia alums are alike. The formula given for these bodies shows that they may be regarded as combinations of a molecule of each of the constituent salts, thus :—

$$\underset{\text{Aluminium sulphate.}}{Al_2(SO_4)_3} + \underset{\text{Potassium sulphate.}}{K_2SO_4} = \underset{\text{'Potash alum.'}}{K_2Al_2(SO_4)_4}.$$

It will be noticed that the formula, $K_2Al_2(SO_4)_4$, may be halved, in which case it becomes $KAl(SO_4)_2$; with twelve molecules of water of crystallisation in the alum molecule. Although this is the simpler molecule, there is one reason for preferring the doubled form, and that is that in all compounds of aluminium of which the vapour-density has been determined, two atoms of aluminium are present in the molecule. The same holds good with iron, another metal which forms 'alums'; the probability is that at least two atoms of aluminium are also present in the alum molecule.

Not only may the potassium of alum be replaced by ammonium, but also other monad metals may perform the same function. The aluminium can also be replaced by other metals of the same valency. In this way an extensive group of double sulphates may be prepared, similar in constitution to alum, and which therefore are termed 'alums.' As may be judged from this definition, they do not all contain aluminium as one of their constituents. The alums are represented by the general formula, $M'M^{vi}(SO_4)_4,24H_2O$. They are isomorphous and generally resemble each other in character.

The following are a few of the more important alums; those which require any further description will be included under their respective metals :—

Potassium alum . . .	$K_2Al_2(SO_4)_4$, $24H_2O$.
Sodium alum . .	$Na_2Al_2(SO_4)_4$, $24H_2O$.
Ammonium alum . . .	$Am_2Al_2(SO_4)_4$, $24H_2O$.
Iron alum	$K_2Fe_2(SO_4)_4$, $24H_2O$.
Chrome potash alum . .	$K_2Cr_2(SO_4)_4$, $24H_2O$.
Chrome ammonia alum . .	$Am_2Cr_2(SO_4)_4$, $24H_2O$.
Manganese alum . . .	$K_2Mn_2(SO_4)_4$, $24H_2O$.

423. Aluminium Silicates.—The simplest of these is ordinary clay, which is essentially a hydrated silicate of alumina, and may be represented by the formula, $Al_2O_3(SiO_2)_2,2H_2O$, or $Al_2Si_2O_7,2H_2O$. The clays are produced by the decomposition of rocks of the felspathic type. Felspar is represented by the formula, $Al_2K_2Si_6O_{16}$; under the influence of carbonic acid dissolved in water a process called 'weathering' proceeds, by which

the felspar is gradually decomposed. The potassium silicate is converted into carbonate, which washes away and leaves behind the silicate of alumina. In a very fine form such aluminium silicate is found near St. Austell, Cornwall, as the result of the decomposition of a species of felspathic granite. It is carefully washed in order to separate it from the quartz and mica present, and then forms a very pure white clay, known as 'China clay' from the first clay of the kind having been imported from that country. The more ordinary forms of clay contain impurities derived from the rocks from which they have been formed; among these, silica, and oxides of iron, lime, and magnesia, are the most commonly occurring.

Properties.—These vary considerably according to the degree of purity of the clay, but the purer forms are, when dry, readily crumbled to a very fine powder. This possesses remarkable absorbent properties, and readily takes up water, by which the clay is converted into a plastic tenacious mass, capable of being worked and moulded into almost any shape. The clay is not soluble in water, and on being broken down in a considerable quantity of it, settles slowly to the bottom and again acquires its plasticity as the excess of water is removed. On being moulded into any particular shape, and then allowed to slowly dry, the clay somewhat hardens and forms a feebly coherent mass. If in this state it be placed in a furnace and very slowly heated it shrinks considerably, and without fusion becomes extremely hard, and although brittle is nevertheless possessed of great strength. Clay is slowly attacked by nitric or hydrochloric acid, but more strongly by sulphuric acid: after ignition all acids except hydrofluoric acid are without action on it. Pure clay is infusible except at the very highest temperatures at our command; the fusing-point is considerably lowered by the presence of impurities.

Industrial Applications.—Clay is used in the preparation of bricks and the manufacture of all kinds of earthenware vessels (reference to which follows). The purer kinds are employed in the preparation of fire-bricks, crucibles, furnaces, and other appliances which are required to be capable of resisting high temperatures.

Other Silicates.—Only passing mention can be given to these, they include felspar already mentioned, and a number of other double or more complex silicates of alumina with various metals. Among these are stilbite, $Al_2O_3CaO(SiO_2)_6$, $6H_2O$; mica, a complex aluminium and magnesium silicate; and chlorite, another mineral containing the same constituents. These and other rock-forming minerals are the components of which most of the great rock masses are constituted.

424. **Pottery.**—Under this term may be included all ware, from the finest porcelain to the coarsest earthen vessels. The difference is due to the varying fineness of the constituents, and the skill expended in their manufacture. Clay of more or less purity is mixed with uncombined silica, in order to counteract the shrinking and liability to crack possessed by pure clay. To give tenacity, some more fusible constituent is added. The mixture is brought into the required shape, dried, and then slowly and carefully heated in a furnace. The articles prepared in this manner are more or less translucent according to the proportion of fusible material introduced into their composition. Those prepared from the finer clays are white, and are known as china ware or porcelain; those from the coarser clays are coloured red or yellow, and known as earthenware. The articles when thus made are dull on the surface and, with the clays free from fusible admixture, porous. To remedy this they are dipped in a glazing material; this consists of some substance which fuses and forms an enamel over the surface of the ware, at a temperature below that at which the ware softens. Fine porcelain is glazed by a mixture of quartz and felspar; coarser earthenware by common salt, this on melting on the vessel in the presence of sand is converted into sodium silicate, which fuses into the ware and renders it impervious.

425. **Glass.**—Closely allied to pottery is glass, which may also contain silicate of alumina, but instead of or in addition to that substance contains also other ingredients. The simplest mode of explanation will be to first give a table showing the percentage composition of various forms of glass.

COMPOSITION OF GLASS

—	1 Hard glass tube	2 Bohemian goblet	3 Window glass	4 Plate glass	5 Bottle glass	6 English flint	7 Optical glass	8 Strass (paste)
Silica	73·13	69·4	66·37	73·85	53·55	51·93	42·5	38·1
Potash	11·49	11·8	—	5·50	5·48	13·77	11·7	7·9
Soda	3·07	—	14·23	12·05	—	—	—	—
Lime	10·43	9·2	11·86	5·60	29·22	—	0·5	—
Alumina	0·30	9·6	8·16	3·50	6·01	0·47	1·8	1·0
Oxide of iron	0·13	—	—	—	5·74	0·27	—	—
Oxide of lead	—	—	—	—	—	33·28	43·5	53·0

Among these the first variety is that known as Bohemian or potash glass, of which silicates of potassium and calcium are the principal ingredients. This form of glass fuses only with considerable difficulty and is employed in the manufacture of the hard glass tubing used in the laboratory for organic combustions and other chemical operations at high temperatures. In the second kind of Bohemian glass, a higher proportion of alumina is present; this glass is more fusible. We next come to window glass, in which the potash is partly or entirely replaced by soda. These glasses are much more fusible. The fifth is ordinary bottle glass, which is made from much coarser material, and contains oxide of iron in large quantity. Flint glass, the composition of which is shown in No. 6, differs from all the others in that lead oxide is an important ingredient, being essentially a silicate of potassium and lead. Glass of this kind is very fusible, brilliant, and takes a high polish. The glass manufactured for optical purposes contains lead in still higher proportions, by which its refractive power is increased. The last, No. 10, shows the composition of the glass employed in the fabrication of imitation jewellery.

The raw materials used for the manufacture of glass consist of fine quartz sand, sodium or potassium carbonates, air-slaked lime, and lead oxide. These materials are selected with great care and mixed in the proportions necessary for the particular glass required. A quantity of old glass or 'cullett' is also added to the mixture. The ingredients are placed either on the hearth of a reverberatory furnace or in large crucibles and

melted down into a tranquil mass, the carbonates being decomposed, with evolution of carbon dioxide gas. The mixture of silicates constitutes a viscous mass, having the properties of a colloid body; in the manufacture of flasks, bottles, globes, and many other articles, the worker avails himself of this viscosity. A sufficient quantity of the molten glass is taken on the end of an iron blowpipe and blown into shape by the mouth, while the glass is in a pasty condition: this shape it retains as the glass cools. Plate glass is prepared by pouring the contents of a crucible of the melted glass on an iron slab, over which a heavy roller is quickly passed, by which the glass is reduced to the desired uniform thickness. Glass is a bad conductor of heat, and in cooling sets first on the outside. The result is that the more slowly cooling parts are in a state of extreme tension as they are attached to the outside which has already solidified, and therefore cannot undergo their normal contraction with the lowering of their temperature. As a result, such glass articles are extremely brittle; in order to remedy this, glass vessels are allowed to cool with extreme slowness in what are called annealing furnaces. In this way, all cools at a uniform rate, and no part of the mass is subjected to tensile strain as the result of unequal contraction. After leaving the furnace, plate glass has its surface first ground flat by the use of emery, and then polished with rouge (an oxide of iron).

Glass, if well made, is practically insoluble in water or acids, except hydrofluoric acid. Nevertheless water dissolves glass in appreciable quantities, a fact which is demonstrated by boiling pure water in a flask for some time and taking the weight before and after the experiment. Weak acids, except sulphuric acid, have less action on glass than water; but the caustic alkalies in solution attack it very readily. In consequence of this, the glass stoppers of bottles containing alkaline solutions are frequently found to be 'set' if the bottles have stood for some time.

Coloured Glass.—The presence of minute quantities of certain metallic oxides imparts definite tints to glass. These are commonly the same as those imparted by the same metals

to a borax bead. Thus cobalt oxide colours glass an intense blue, and chromium compounds give a green tint. Cuprous oxide, Cu_2O, produces a red tint, while a magnificent ruby colour is occasioned by the addition of a compound of tin and gold oxides (purple of Cassius.)

426. **Other Salts of Aluminium.**—Among these may be reckoned the sulphide, Al_2S_3, produced by the action of sulphur on metallic aluminium. Soluble sulphides, as that of ammonium, do not precipitate aluminic sulphide, but the hydrate, $Al_2(HO)_6$. The halogen salts—bromide, iodide, and fluoride—have formulæ corresponding to that of the chloride, and like it are volatile bodies, whose density has been determined in the vaporous state.

Aluminium phosphates occur as constituents of the turquoise and other minerals.

Iron.—Symbol, Fe. Atomic weight, 55·9.

427. **Occurrence.**—Minute quantities of iron in the free state occur disseminated throughout basaltic rocks: larger masses are found native, which undoubtedly are of meteoric origin. These bodies vary considerably in size; one of the largest ever found was discovered in Peru, and has an estimated weight of about fifteen tons. Meteoric iron is usually alloyed with cobalt, nickel, and other allied metals.

In combination, iron is most widely diffused, both through aqueous and igneous rocks; a number of minerals are definite compounds of iron; among these are the oxides, carbonates, sulphides, and arsenides. The latter are not worked for iron, because of the difficulty of removing the sulphur and arsenic from the metal; traces of these bodies seriously impair the quality of iron in the metallic state. The ores, or workable sources of iron, include the following:—

Magnetic Iron Ore, *Magnetite*—composition, Fe_3O_4—contains 72 per cent. of iron; occurs principally in Norway, Sweden, Russia, and North America.

Red Hæmatite—composition, Fe_2O_3—contains 70 per cent. of iron; is found largely in this country, occurring in peculiar, red, kidney-shaped masses.

Specular Iron Ore is similar in composition to red hæmatite, but is very hard and crystalline. Occurs in Russia and Spain.

Brown Hæmatite—composition, hydrated oxide of iron—may be represented by $Fe_2(HO)_6$; contains about 60 per cent. of iron. Occurs in Cumberland, and is an important French ore of iron.

Spathic Iron Ore—composition, $FeCO_3$—contains 48 per cent. of iron. In appearance this ore resembles crystalline calcium carbonate.

Clay Iron Stone is a mixture of iron carbonate with clay in various proportions, from the pure spathic ore to ferruginous clays. The percentage of iron in workable ores varies from 17 to about 50 per cent. This is the most important British iron ore. *Black band ore* is a sub-variety, which contains coaly or bituminous matter in addition to clay ironstone.

Iron compounds are also found in soils, from which they are absorbed by plants, and from these in turn by animals, of whose blood iron is an important constituent.

428. **Theory of Extraction.**—From the theoretic point of view the most interesting method of obtaining iron is that practised in Spain, and known as the Catalan process. The ores employed are very pure, and consist of magnetite and hæmatite. Evidently, all that is necessary for the production of pure iron is the removal of oxygen from the ore. The agent used for this purpose is carbon, which at a sufficiently high temperature combines with and removes the oxygen from iron oxides. But, further than this, carbon and iron somewhat readily unite, and the presence of carbon in iron exercises a most remarkable effect on the general character of the metal. The furnace used for the Catalan process is shown in fig. 72. The hearth is from 17 to 20 inches in dimensions each way, and is built of masonry with a granite block for the bottom, and lined with iron. Through the pipe T, known technically as a tuyère (*Anglicè*, twyer), is introduced a blast of air. The ore is broken into lumps and a coarse powder, termed *greillade*. The furnace is heated by charcoal, the side nearest the twyer being charged with a mixture of *greillade* and charcoal, and the

lumps of ore placed on the opposite side. The combustion of the charcoal, in the excess of air introduced by the blast, produces carbon monoxide, and by this the iron is reduced to the metallic state with the formation of carbon dioxide. The *greillade* in the charcoal mixture near the twyer descends towards the bottom of the hearth in a fused state, having formed a 'slag' (molten silicate of iron) by combination with the silica present as impurity in the ore. The lumps of ore will meantime be reduced to iron, and in the presence of the gases of the furnace this iron will be *carburised* (that is, caused to combine with carbon). This carburised iron slowly descends to the bottom of the furnace, and there meets with the slag, when a mutual reaction ensues, resulting in the carbon from the iron combining with the oxygen of the iron oxide in the slag, forming carbon oxide, which escapes and leaves comparatively pure iron behind, underneath a layer of slag. From this the iron is taken as a spongy mass, and consolidated by a series of blows from a heavy hammer. An important point in this process is the decarburisation of the iron by the *greillade* slag rich in oxide. Now, if in this operation less *greillade* had been employed, the result would be a more highly carburised iron. Now iron which contains a small percentage of carbon is known as steel; and, accordingly, by the Catalan process steel is produced by making less *greillade* slag, tapping it off more frequently, and so arranging the blast as to get the maximum amount of carburisation.

FIG. 72.

The Catalan forge does not admit of a higher temperature,

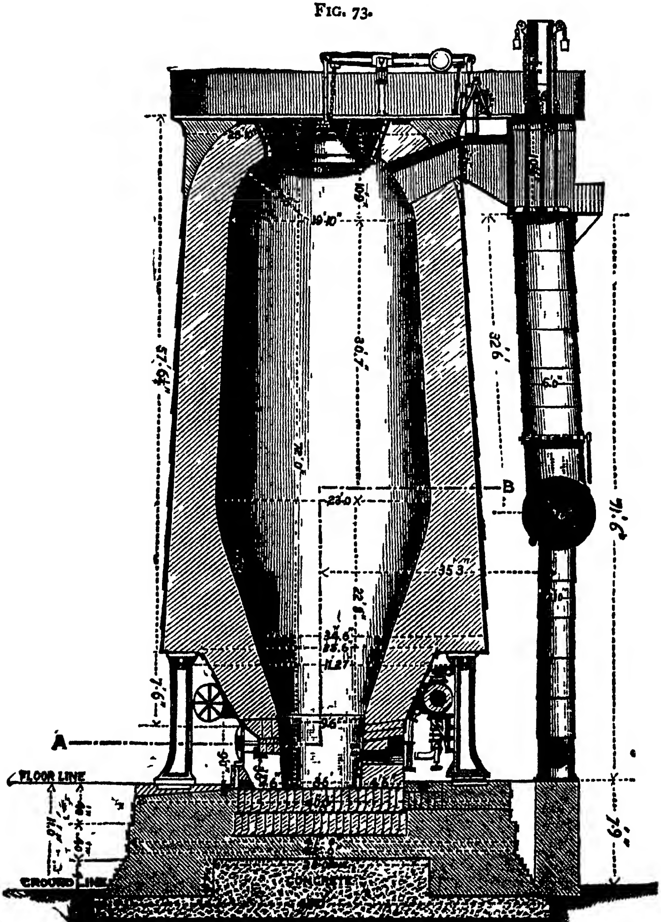
but the same species of reaction, occurring with the temperature higher, results in the iron taking up more carbon, and also dissolving silicon and other impurities by which it is converted into cast iron.

429. English Methods of Iron-smelting.—In this country the processes of iron-smelting resolve themselves into (1) the extraction of cast iron direct from the ore, (2) the preparation of pure or wrought iron by the puddling process, (3) the carburisation of pure iron to form steel.

Cast Iron.—The iron ores are usually first gently roasted in order to expel carbon dioxide gas and water. They are then smelted together with a flux and some fuel in a special form of furnace known as a blast-furnace. One of these, of the most modern construction, is shown in fig. 73. The dimensions are throughout marked in the figure. This furnace essentially consists of a structure of best fire-bricks, enclosed within a casing of riveted wrought-iron plates. The total height of the furnace is about 80 feet, and the greatest internal diameter 23 feet. The very lowest part of the furnace, almost rectangular in section, is termed the hearth or crucible; from the crucible to the widest part of the furnace is called the *boshes*. Above, the furnace is almost parallel until the considerable constriction at the top. Into the furnace, through the sides of the hearth, the tuyères, of which there are three, enter on the three sides of a square. On the other side is the *dam*, through which the molten iron and slag are drawn off from the furnace. Modern furnaces are now almost universally supplied with arrangements by which the air-blast is heated before it enters the furnace. For this purpose the enormous volumes of carbon monoxide produced during the reduction of the ore, are drawn off through the large pipe to the right of the figure, and employed to alternately heat two series of brick chambers. The one series of chambers being hot, the gases are diverted to the other, and air is heated by being passed through it. After a time the air and inflammable gases are changed over, so that each series of chambers is alternately heated, and then becomes a source of heat to the blast, which enters the furnace at a temperature of

from 350° to 700° C. The charge or 'burden' of the furnace consists of the roasted ore, fuel (which may be coke or very

Fig. 73.



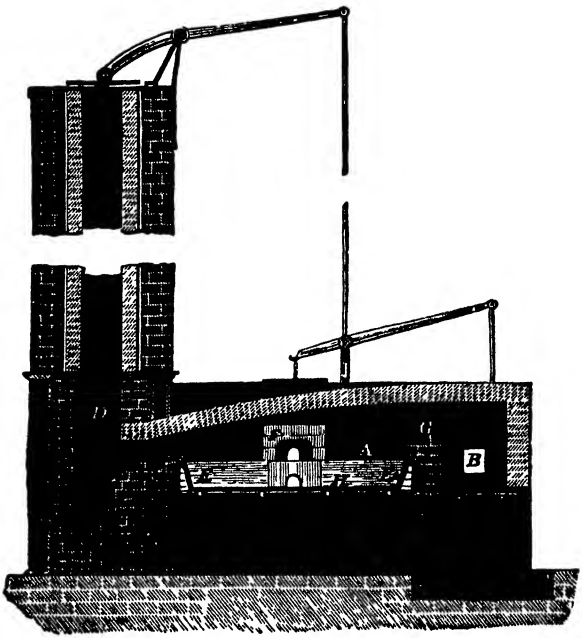
hard coal), and flux. The nature of the latter depends on the character of the impurities present in the ore. If silica or clay be present in excess, limestone is added, which forms a fusible

slag or glass with these substances; on the other hand, if excess of lime be present in the ore, siliceous substances may be added. Different kinds of ore may sometimes be mixed with advantage, so that the impurities of the one act as the complement to those of the other in producing a slag. The mixed materials are continuously being added through the cup-and-cone arrangement shown at the top of the furnace, and slag and iron, known as 'pig,' are drawn off from the bottom. The blast on first entering the furnace forms carbon dioxide with the fuel; this, in passing upward through the glowing carbon, yields carbon monoxide, which is the effective reducing agent. The descending ore, as it gets into the hotter part of the furnace, is first reduced to spongy iron by the carbon monoxide, and is coated over by a film of liquid slag. At a lower zone of the furnace, where the temperature is higher, the iron is carburised. Below this point the iron begins to absorb sulphur from the coke present; and still lower, where it is subjected to a greater heat, the phosphates in the ore are reduced to phosphorus by the carbon, and this is taken up by the iron. Approaching the hearth the temperature is sufficiently high to completely melt the pasty iron, which also absorbs silicon produced by reduction of silicates. In the hearth a layer of molten iron occurs underneath the fused slag. This is drawn off and run into moulds some three or four inches wide and deep, and from three to four feet in length.

Wrought Iron.—In order to remove the impurities from cast iron, it is subjected to a process termed 'puddling.' This operation is conducted in a reverberatory furnace, such as is shown in fig. 74, and is known as a puddling furnace. At B is the furnace, in which is burnt as fuel a variety of coal capable of producing long flames; at G is the fire-bridge, and at C the flue-bridge, and between them is the hearth, A. These furnaces are lined with a mixture called *fettling*, an essential ingredient of which is pure hæmatite ore. The cast iron is placed on the hearth of the furnace and slowly melted, when, after a time, it undergoes ebullition through the carbon of the iron combining with the oxygen in the hæmatite. Toward the close of this

boiling, the workman stirs the molten iron by means of an iron rod; gradually the iron becomes pasty, and collects in a mass on the end of the stirring-rod; by skilful manipulation this mass is increased by accumulating the masses of spongy iron

FIG. 74.



disseminated through the charge. Finally, the whole of the iron present is thus collected into some four or five such masses, called 'blooms'; these are taken while hot to a massive steam hammer, and there wrought into compact ingots. These are next taken to a powerful series of rolls, and elongated into bars, in which the iron has a fibrous structure. In the puddling furnace not only the carbon, but also the phosphorus, silicon, and sulphur, are removed, these being dissolved from the iron and remaining in the slag, which consists of ferrous silicate, containing phosphorus and sulphur.

Steel Manufacture.—Steel is obtained from good wrought iron by a process known as cementation. Iron bars are packed in a furnace filled with powdered charcoal, and are then raised to a red heat, which is maintained for some five or six days. At the end of that time the iron is slowly allowed to cool, and on withdrawal from the furnace is found covered with blisters; hence the name blister-steel. Although the iron has not been melted at the temperature employed, yet it is found to be carburised throughout its whole mass.

Bessemer steel is prepared by first burning the silicon and carbon out of pure varieties of cast iron. This is effected in vessels known as converters. Molten iron is run into the converter, and then a blast of air forced through it from the bottom. The temperature rises considerably as a result of the combustion of carbon and silicon, and part of the iron; the flame produced is watched spectroscopically until the iron is sufficiently pure. A special make of cast iron known as *spiegeleisen*, is used for the purpose of adding carbon to the purified iron; spiegeleisen contains carbon and manganese, but is free from other cast iron impurities. A quantity of this in the melted condition is added, sufficient to convert the iron into steel, which is cast into ingots.

Many other processes are employed in the production and manufacture of iron and steel; but, for description of these, works on metallurgy must be consulted.

430. Preparation of chemically pure Iron.—To prepare iron in this form, filings of the purest bar iron may be mixed with pure ferric oxide, covered over with powdered glass as a flux, and heated in a crucible. The oxygen of the ferric oxide burns off the traces of carbon and silicon, and the excess forms with the glass a slag. A button of pure iron remains. Or the pure oxide may be reduced by heat in a current of hydrogen.

431. Properties.—Wrought iron, steel, and cast iron possess properties so distinct as to cause them to be as far apart in many physical characters as though they were different

metals. The above represents their order of chemical purity, in which they will be described.

Wrought Iron.—This form approximates to chemically pure iron in general properties. Iron has a greyish-white colour, and is susceptible of a high polish. In the pure state it possesses only a moderate degree of hardness and great tenacity; when broken the structure is usually fibrous. Wrought iron may be bent and more or less worked when cold, but on being heated it becomes softer, and may be forged or rolled into almost any desired shape. At a white heat iron becomes sufficiently soft and pasty for two pieces to be welded into one solid mass by a series of rapid blows. It is only at the most intense heats that iron actually melts.

Iron is susceptible of magnetism in a far greater degree than any other substance; its magnetism in the pure state is not, however, permanent. In the finely divided state, as when prepared by the reduction in hydrogen of the oxide, iron takes fire spontaneously on coming in contact with air. Small particles burn with brilliant scintillations when heated, hence iron filings are used in fireworks. At ordinary temperatures polished iron retains its lustre in dry air, but in the presence of moisture and carbon dioxide commences to oxidise or rust. The oxide of iron thus formed is pervious to air, and so when rusting has once commenced it proceeds rapidly. In water absolutely free from air and carbon dioxide, iron undergoes no change, and remains bright; but at a red heat iron decomposes water, with copious evolution of hydrogen. The halogens attack iron somewhat readily, especially in the presence of water. Iron is dissolved by hydrochloric and dilute sulphuric acids, with the evolution of hydrogen gas.

Iron may be made to assume a passive condition by various modes of treatment; thus, on being immersed in nitric acid of specific gravity 1·45, the iron acquires the property of being able to resist the action of nitric acid of a specific gravity of 1·35, although, ordinarily, acid of that strength attacks it vigorously. Momentary exposure to a spirit-lamp flame also induces the same passive condition, which is not, however, per-

manent, for simple contact with an ordinary wire may destroy the passivity of the heated piece. It is probable that this condition is due to the formation of a thin coating of oxide. A process has been patented in which iron articles are coated by a protective coating of magnetic oxide, Fe_3O_4, by exposure to a current of steam at a red heat.

Steel.—This is essentially a compound of iron with varying proportions of carbon. Steel has a granular or crystalline structure, as distinguished from the fibrous nature of wrought iron. The character of steel varies, according to the proportion of carbon present. Steel is much more readily fusible, and the less carburised varieties still retain the capacity for being welded at a white heat and forged when red-hot. On being heated to redness and then suddenly cooled by dipping in water, steel becomes intensely hard; while if, on the other hand, it be cooled slowly it is nearly as soft as wrought iron. This enables steel to be employed in the manufacture of all kinds of cutting implements. It is wrought in the soft state, and then hardened by sudden cooling. In this extremely hard state the steel is very brittle; its hardness may be diminished and its toughness increased by the process of tempering, in which the hard steel is slightly heated and then allowed to cool. Steel possesses a much higher tensile strength than wrought iron, and is, in fact, the strongest material known. Steel can not only be magnetised, but permanently retains the magnetism, and is thus used for making permanent magnets. On dissolving soft steel in acids a black residue remains, consisting of graphitic carbon, but hardened steel entirely dissolves, producing a dark-coloured solution, owing to the presence of hydrocarbons. The depth of this colour in solutions of definite strength affords a means of estimating the quantity of carbon present in the steel.

Cast Iron.—In this form iron contains more carbon than is present in steel; also there are present, as impurities, silicon, phosphorus, sulphur, and often small quantities of other metals—as, for example, manganese. Cast iron varies considerably in quality, according to the proportion of carbon, and whether or not the carbon is in the combined condition. With less carbon, the iron is soft and grey; higher proportions

produce a whiter, harder, and more fusible iron. Rapid cooling causes iron to become whiter, harder, and more brittle. Cast iron is brittle, and may be fractured by blows from a hammer. It melts to a mobile liquid condition, and consequently can be run into moulds of almost any form, and acquires and retains their shape on cooling. It cannot be either forged or welded. It is sufficiently soft to be easily filed and shaped in lathes and other cutting machines. On solution in acids, the grey cast iron leaves a residue of graphite, while the whiter varieties dissolve entirely in a similar manner to steel.

The following table gives the percentage composition of different varieties of wrought iron, steel, and cast iron:—

DESCRIPTION	Fe	Mn	Cu	Carbon		Si	S	P
				Combined	Graphitic			
WROUGHT IRON								
Swedish	99·863	trace	—	0·054	—	0·028	0·055	trace
Russian	99·412	0·02	—	0·272	—	0·062	0·234	—
Welsh	97·72	–	—	—	—	0·26	0·21	0·71
Lowmoor	99·372	0·28	—	0·16	—	0·122	0·104	0·106
STEEL								
Rails	—	0·264	—	0·150		0·091	0·025	0·032
Boiler plate	—	0·273	—	0·300		0·056	0·040	0·041
Bessemer metal, Dowlais	—	0·576	0·025	0·490		0·009	0·033	0·036
Cast steel, Sheffield	—	—	—	0·950	0·220	—	—	—
Cement steel, English	98·093	—	—	1·807	—	0·100	—	—
" " Sheffield	—	0·120	—	0·627	0·102	0·030	0·005	0·000
CAST IRON								
Grey iron, Dowlais	94·36	0·50	—	0·04	3·10	2·16	0·11	0·63
Charcoal, mottled	93·691	1·426	—	0·532	3·768	0·432	0·151	trace
Coke, hot blast, mottled	94·45	—	—	0·72	2·28	1·35	0·03	1·47
White iron, Durham	93·183	2·370	0·014	4·100	—	0·230	0·030	0·073
Spiegeleisen	88·56	5·75	0·16	5·04	—	0·41	0·08	0·00

432. Industrial Applications.—Iron, in its various forms, constitutes the raw material of the engineer and toolmaker. Its uses in the arts are so extensive that even their simple enumeration would demand more space than is at our disposal.

433. Oxides and Salts of Iron.—Iron forms three oxides, of which the following are the formulæ:—

Ferrous oxide . . .	FeO.
Ferric oxide	Fe_2O_3.
Ferric tetroxide, or magnetic oxide	Fe_3O_4, or FeO,Fe_2O_3.

The former two of these are basic, and yield two well-marked series of salts, known respectively as ferrous and ferric salts. The last is a neutral oxide, and is viewed as a compound of the two preceding. Certain salts are known in which iron behaves as an acid-forming compound; these are termed ferrates, but the hypothetic anhydride, FeO_3, has not as yet been obtained.

434. **Ferrous Chloride, $FeCl_2$.**—In the dry way, this salt is formed by passing hydrochloric acid gas over red-hot iron filings. It is a white powder, and may be sublimed without decomposition. Hydrochloric acid in solution dissolves iron, with evolution of hydrogen and formation of this chloride, which crystallises out in crystals, having the composition $FeCl_2,4H_2O$. Ferrous chloride, in common with most other ferrous compounds, is readily converted by oxidising agents into the corresponding ferric compound. In all probability, the true formula of this body is at least Fe_2Cl_4, and probably an even higher multiple of $FeCl_2$.

435. **Ferric Chloride, Fe_2Cl_6.**—On passing chlorine gas over ignited metallic iron, both being in the dry state, this compound is formed; it passes over and condenses as brown anhydrous crystals, which are very deliquescent. The salt is of interest, as being one of the iron compounds whose vapour-density has been determined. In the wet way, ferric chloride is formed by dissolving the corresponding oxide in hydrochloric acid. In an indifferent atmosphere, such as that of nitrogen or carbon dioxide, both basic iron oxides dissolve in hydrochloric acid, with the formation of their corresponding chlorides.

436. **Ferrous Oxide, FeO.**—On adding potassium hydrate to a solution of pure ferrous sulphate, in the absence of air, a white precipitate of ferrous hydrate, $Fe(HO)_2$, is formed. On boiling the solution, still in the absence of air,

the hydrate loses its water and is converted into the oxide. The hydrate absorbs oxygen with great readiness, and becomes changed into the ferric compound, $Fe_2(HO)_6$, at the same time passing through gradations of colour, from pale to dirty green, and then the reddish tint of the ferric compound. Ferrous oxide forms the series of salts termed ferrous salts, which, by absorption of oxygen, become changed into ferric compounds.

437. **Ferric Oxide, Fe_2O_3.**—This oxide occurs plentifully in nature, both in the anhydrous and hydrated form. It may be obtained by igniting ferrous sulphate, and, under the names of colcothar and rouge, is used as a polishing material for jewellery and also plate glass. The hydrate, $Fe_2(HO)_6$, is readily precipitated from a solution of the chloride, Fe_2Cl_6, by the addition of ammonia, when it forms a bulky reddish-brown precipitate. This, on being heated, loses its water, and is converted into ferric oxide. The hydrate dissolves readily in acids, forming ferric salts; the ignited oxide is only slowly attacked even by concentrated acids. At present the hydrate is employed in gasworks as an absorbent of sulphuretted hydrogen; the corresponding sulphide, Fe_2S_3, also in a state of hydration, is formed. On passing air through the compound, the oxide is again produced, and sulphur deposited.

438. **Magnetic Iron Oxide, Fe_3O_4.**—This oxide is found in nature as the mineral termed magnetite, distinguished by its natural property of permanent magnetism. It is formed by passing steam over red-hot iron, and then adheres to the surface of any iron article thus treated. On solution in hydrochloric or sulphuric acids, this oxide dissolves, with the formation of a mixture of ferrous and ferric salts.

439. **Ferrous Sulphide, FeS.**—This body may be formed by bringing together white-hot iron and sulphur, or by precipitating ferrous sulphate with sulphuretted hydrogen in the presence of an alkali. The sulphide evolves sulphuretted hydrogen when treated with sulphuric or hydrochloric acid.

440. **Ferric Sulphide, FeS_2.**—In this form iron largely occurs in nature, either in the massive state or in very perfect

cubical or other crystals of the cubic system. It has usually a very bright, brassy, metallic lustre, and is termed iron pyrites or mundic. On being heated the sulphide evolves sulphur, and so is frequently termed sulphur ore, for which element it is extensively worked as a part of the process of sulphuric acid manufacture. Pyrites is not affected by cold sulphuric or hydrochloric acid, but may be dissolved by nitric acid, when the sulphur separates in the plastic state.

441. **Ferrous Sulphate, $FeSO_4,7H_2O$.**—On heating 'alum schists' containing pyrites, sulphates of alumina and iron are formed. On lixiviation and subsequent crystallisation ferrous sulphate separates as greenish crystals, of the formula given above. By the action of heat the water is driven off, and finally the salt itself is decomposed. This sulphate is soluble in water, and, with tannin and other allied organic bodies, forms ink and other black dyes. Ferrous sulphate in solution absorbs large quantities of nitric oxide, thus yielding a dark brown liquid. This reaction is employed as a test for nitric acid and the nitrates. Ferrous sulphate, both in the solid state and in solution, somewhat readily oxidises, with the formation of ferric sulphates.

442. **Ferric Sulphate, $Fe_2(SO_4)_3$.**—By oxidising ferrous sulphate in the presence of sulphuric acid, this compound is obtained. For this purpose the solution is gently warmed and small quantities of nitric acid added. Ferric sulphate is deliquescent, and combines readily with ammonium sulphate, forming an iron alum, which crystallises readily, and is isomorphous with ordinary alum. Ferric sulphate readily forms basic hydrated sulphates of various compositions. These are only slightly soluble in water, hence the deposit gradually formed when a solution of ferrous sulphate becomes oxidised.

443. **Ferrous Carbonate, $FeCO_3$.**—This salt, mixed with clay, is the most plentiful of the British iron ores. When crystallised it is isomorphous with calcium carbonate, and is soluble in water containing carbonic acid; such water forms what are known as chalybeate springs. The carbonate may be

formed by precipitation, but is unstable, giving up its carbon dioxide and forming ferric oxide.

Ferric oxide, being a weak base, is apparently unable to combine with such a weak acid as carbonic acid, for no ferric carbonate is known in the solid state.

444. **Iron Silicates.**—These are largely produced as slags in various metallurgical operations on iron. Not only the silica, which is a constituent of the ore, but also the burnt clay of which crucibles and bricks are formed, is energetically attacked by fused oxide of iron. Ferrous silicate may be represented by the formula, Fe_2SiO_4.

445. **Other Salts of Iron.**—Iron forms a ferrous bromide and iodide, used more or less in medicine, and bearing some resemblance to the chloride. Both ferrous and ferric nitrates are known, but possess no special importance. Normal ferric phosphate is formed by precipitation of ferric chloride with sodium phosphate; it is yellowish-white, and is insoluble in water, but soluble in acids.

446. **Cyanogen Compounds of Iron.**—Iron forms with cyanogen a remarkable series of compounds, which may be viewed as combinations of hydrocyanic acid with iron cyanide to form more than one distinct acid. Thus, for example, we have hydroferrocyanic acid, H_4FeCy_6, which may be otherwise written as $(HCy)_4FeCy_2$. These acids are best known in their combinations as salts.

Ferrocyanides.—Thus on heating together nitrogenous organic refuse (blood, &c.), caustic potash, and iron filings, and subjecting the resultant mass to lixiviation, a liquid is obtained which yields on evaporation beautiful transparent yellow crystals, having the composition $K_4FeCy_6,3H_2O$. These are potassium ferrocyanide, known commercially as yellow prussiate of potash. This is a very stable salt, and, although so largely composed of potassium cyanide, is not poisonous, showing that the compound is a well-marked chemical body possessing new and distinctive properties of its own. The ferrocyanide is soluble in water, and on addition of

hydrochloric acid in the cold yields the free acid, H_4FeCy_6, which crystallises as a white powder. On heating the potassium ferrocyanide with dilute sulphuric acid, hydrocyanic acid, HCy, distils over. With concentrated sulphuric acid, the cyanogen radical is broken up, carbon monoxide and ferrous and ammonium sulphates being formed.

Potassium ferrocyanide yields with ferric chloride a dark blue precipitate of Prussian blue, which has the formula $(Fe_2)_4(Fe_2)_3(C_3N_3)_{12}$. This is insoluble, but a soluble variety is also known, prepared by adding a solution of the iron salt to excess of ferrocyanide, and washing the precipitate until free from potassium salts. At this stage the washing water is coloured blue, and what remains is Prussian blue in a soluble form.

With copper salts a chocolate-brown copper ferrocyanide is formed, having the composition Cu_2FeCy_6.

Ferricyanides.—On passing chlorine into a solution of potassium ferrocyanide until a portion of the solution no longer gives a blue precipitate with ferric chloride, the following change will have occurred:—

$$\underset{\text{Potassium ferrocyanide.}}{2K_4FeCy_6} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Potassium chloride.}}{2KCl} + \underset{\text{Potassium ferricyanide.}}{K_6Fe_2Cy_{12}}.$$

On concentration dark red crystals of the ferricyanide, commonly known as red prussiate of potash, crystallise out. Potassium ferricyanide produces no precipitate with ferric salts, but with soluble ferrous compounds yields a dark blue precipitate of what is called Turnbull's blue, having the following composition, $Fe_3Fe_2Cy_{12}$.

Chromium.—Symbol, Cr. Atomic weight, 52·4.

447. **Occurrence.**—Chromium does not occur in the free state in nature, but is found as lead chromate, crocoisite, $PbCrO_4$, and chrome iron ore, $FeOCr_2O_3$.

448. **Preparation and Properties.**—By reduction of the oxide with charcoal from sugar, chromium is obtained in small crystals of about the same hardness as corundum. The metal melts more difficultly than platinum, but burns when

heated in the oxyhydrogen blowpipe flame, forming the oxide, Cr_2O_3. The chloride may be formed from the metal either by the action of chlorine or hydrochloric acid. Nitric acid is without action on the metal, which, however, on ignition with either potassium nitrate or chlorate is converted into the chromate.

449. **Compounds of Chromium.**—Chromium forms several oxides, of which the most important are—

Chromous oxide, CrO.
Chromic oxide, Cr_2O_3.
Chromic anhydride, CrO_3.

The first of these is very unstable, rapidly absorbing oxygen and being converted into the next higher oxide. Chromic oxide is basic in properties, and forms the principal salts of chromium. Chromic anhydride, CrO_3, forms a corresponding acid and a very important series of salts.

450. **Chromous Compounds.**—These are so unstable that their preservation in the pure state is a matter of difficulty.

Chromous Chloride, $CrCl_2$, is obtained by reducing chromic chloride in a current of hydrogen, by the action of heat. It is a white substance, soluble in water, and readily oxidised to a green solution of chromic chloride in the presence of atmospheric oxygen.

Chromous Oxide, CrO, is only known in the hydrated condition, and is formed as a dark brown precipitate by the action of potassium hydrate on a solution of chromous chloride. It decomposes water with evolution of hydrogen.

451. **Chromic Chloride, Cr_2Cl_6.**—By passing chlorine over a mixture of chromic oxide and charcoal at a red heat in a glass tube chromic chloride is formed, and condenses in the cooler parts of the tube as violet-coloured crystals. Prepared in this manner, chromic chloride is insoluble in sulphuric, nitric, and hydrochloric acids, although prolonged boiling with water effects their solution. A green chloride is also formed in the wet way by dissolving chromic oxide in hydrochloric acid.

452. Chromic Oxide, CrO_3.—The addition of ammonia to a solution of chromium sulphate results in the precipitation of chromic hydrate, $Cr(HO)_6$. This, on being ignited, is converted into the oxide, which is insoluble in acids. The oxide may also be obtained by exposing the vapour of chromium oxychloride, CrO_2Cl_2, to a red heat; the crystals thus formed are of great hardness. Prepared by this and other 'dry' methods, chromic oxide is used as a green pigment in china-painting.

Chrome Ironstone, $FeOCr_2O_3$, is a body closely resembling magnetic iron ore in composition, being such ore with the ferric oxide replaced by chromic oxide. It is isomorphous with magnetite, attacked very slowly by the most concentrated acids, and infusible at the highest furnace heats. On being heated with potassium carbonate and chlorate, the chromic oxide is oxidised to chromate.

453. Chromic Oxydichloride, CrO_2Cl_2.—On heating together a mixture of potassium bichromate, sodium chloride, and sulphuric acid, the following reaction occurs :—

$$\underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} + \underset{\text{Sodium chloride.}}{4NaCl} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Chromic oxydichloride.}}{2CrO_2Cl_2} + \underset{\text{Sodium sulphate.}}{2Na_2SO_4} + \underset{\text{Water.}}{3H_2O}.$$

Dense red fumes of the chromium compound distil over, and may be condensed to a blood-red liquid, which, on being treated with water, is decomposed into chromic and hydrochloric acids.

454. Chromic Sulphate, $Cr_2(SO_4)_3$.—This body is remarkable on account of its forming three distinct modifications. It may be obtained by mixing together sulphuric acid and chromic hydrate, and exposing the mixture to the air; gradually water is absorbed and a blue liquid formed, which, on the addition of alcohol, deposits a crop of octahedral crystals, having the composition, $Cr_2(SO_4)_3,15H_2O$. This solution, on being boiled, becomes green, and on evaporation, and elevation of the temperature to 370° C., becomes anhydrous

and yields a red form of the salt, which is insoluble in water and acids.

Chrome Alum, $K_2Cr_2(SO_4)_4, 24H_2O$, is formed by the addition of the equivalent quantity of potassium sulphate to the blue modification of chromic sulphate: it crystallises readily in forms isomorphous with ordinary alum, forming purple crystals, which dissolve in cold water to a solution of the same tint. But on raising the temperature to 70° C., the colour changes to green, with probably decomposition of the 'alum' and production of the green chromium sulphate. In this state the solution will not crystallise, but on prolonged keeping (some months) gradually resumes its purple tint, and deposits chrome alum crystals. Chrome alum is formed as a waste product in the working of bichromate voltaic batteries, as a result of the reduction by nascent hydrogen of potassium bichromate in the presence of sulphuric acid:—

$$\underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} + \underset{\text{Sulphuric acid.}}{4H_2SO_4} + \underset{\text{Nascent hydrogen.}}{6H} = \underset{\text{Chrome alum.}}{K_2Cr_2(SO_4)_4} + \underset{\text{Water.}}{7H_2O}$$

It also occurs as a bye product in the manufacture of alizarin. Chrome alum is employed in calico-printing and dyeing, and also in certain modern processes for tanning leather.

455. Chromic Acid and Chromates.—Chromic anhydride, the highest known oxide of chromium, possesses powerful acid properties, and is prepared by the action of sulphuric acid on a chromate. If concentrated sulphuric acid be poured into a cold saturated solution of potassium bichromate, $K_2Cr_2O_7$, the following reaction occurs:—

$$\underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Chromic anhydride.}}{2CrO_3} + \underset{\text{Water.}}{H_2O}.$$

The water is retained by the excess of sulphuric acid used, and chromic anhydride separates as ruby-red acicular crystals. These should be placed to drain on a dry porous tile *in vacuo*. The adherent sulphuric acid may be removed by washing with pure nitric acid, and then aspirating a current of dry air through the crystals. The substance is deliquescent, and dis-

solves in water with the production of chromic acid, H_2CrO_4. It should be noticed that the formulæ of the anhydride and acid are similar to those of the corresponding sulphuric compounds. The acid is readily reduced to chromic oxide, Cr_2O_3, or its salts, by various reducing agents.

Potassium bichromate, $K_2Cr_2O_7$, or $K_2CrO_4CrO_3$, is the starting point in the manufacture of the chromates, and, in fact, most of the other chromium compounds. On fusing chrome ironstone with potassium carbonate, and either nitrate or chlorate, the following reaction (leaving out of consideration the further oxidation of the iron) occurs :—

$$\underset{\text{Chrome ironstone.}}{FeOCr_2O_3} + \underset{\text{Potassium carbonate.}}{K_2CO_3} + \underset{\text{Potassium chlorate.}}{KClO_3} = \underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Iron oxide.}}{(FeO)}.$$

The mass on cooling is found to have acquired a bright yellow colour. On the large scale the chlorate is dispensed with, and the ore and carbonate mixed with chalk to render it porous when hot. The mixture is heated in a reverberatory furnace, and stirred about so as to oxidise it by atmospheric oxygen. The residual mass is lixiviated and potassium carbonate added, if necessary, to decompose any calcium chromate; sufficient sulphuric or nitric acid is added to the solution to ensure the production of the bichromate, and the liquid evaporated ; fine orange-coloured crystals of the salt separate out. Potassium bichromate is soluble in water, forming a solution which has an acid reaction. The salt is used in bichromate batteries as a source of oxygen, and also in dyeing and calico-printing.

Potassium bichromate has a composition analogous to that of the double sulphate of sodium, $Na_2S_2O_7$, and also Nordhausen sulphuric acid, $H_2S_2O_7$. Not only is there the bichromate of potassium, $K_2O(CrO_3)_2$, just described, but by evaporating a solution of this salt with nitric acid the trichromate, $K_2Cr_3O_{10}$, or $K_2O(CrO_3)_3$, and a tetrachromate, $K_2Cr_4O_{13}$, or $K_2O(CrO_3)_4$, may be formed. These are crystals of a full red and crimson colour.

Potassium Chromate, K_2CrO_4.—On adding potassium carbonate to the bichromate the following reaction occurs :—

$$\underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} + \underset{\text{Potassium carbonate.}}{K_2CO_3} = \underset{\text{Potassium chromate.}}{2K_2CrO_4} + \underset{\text{Carbon dioxide.}}{CO_2}.$$

This is a salt of a pale yellow colour, but of great tinctorial power, very soluble in water, from which it is crystallised only with difficulty, as somewhat deliquescent crystals. Potassium chromate is alkaline in reaction, and is decomposed by even such a weak acid as carbonic acid, the bichromate and a carbonate being formed.

Lead Chromate, $PbCrO_4$, is of interest as being the native substance in which chromium was first discovered. It may be prepared by precipitating lead acetate with potassium chromate. When dried it forms a pigment of a pale yellow tint known as chrome yellow. This is used also as a dye in calico-printing. Lead chromate evolves oxygen on being heated with organic substances, and therefore is sometimes used in organic analysis instead of copper oxide.

456. Other Chromium Compounds.—In addition to the chromium salts already described, several others, including the nitrate, $Cr_2(NO_3)_6$, are known. Chromium forms an interesting fluoride, having the composition, CrF_6 which is volatile, and at a low temperature is condensed to a blood-red liquid. Chromic acid also forms a well-marked series of chromates with most of the metals. In addition to those described, silver chromate, Ag_2CrO_4, and barium chromate, $BaCrO_4$, are the most noticeable.

Manganese.—Symbol, Mn. Atomic weight, 54·8.

457. Occurrence.—Manganese occurs principally as the dioxide, MnO_2, which constitutes the mineral pyrolusite, and is widely distributed.

458. Preparation and Properties.—Metallic manganese may be obtained by heating the carbonate with sugar-charcoal for about two hours at the highest temperature of a wind furnace. In this way a button of metal is formed, which contains, however, considerable quantities of carbon. From this it may be in great measure freed by re-fusion with more manganese carbonate. The metal thus produced is in appear-

ance somewhat similar to cast iron, being brittle, moderately hard, and crystalline. Manganese quickly absorbs oxygen from the air, and also decomposes warm water, with evolution of hydrogen. It requires to be preserved either in sealed tubes, or, like sodium, under naphtha. It is quickly dissolved by dilute acids. Manganese has no practical applications in the pure state, but spiegeleisen, already referred to, is a cast iron containing high percentages of manganese. Small quantities of this metal in steel are said to improve its quality, perhaps indirectly, by assisting in the removal of injurious impurities.

459. Compounds of Manganese.—Manganese forms several distinct series of compounds, of which the following oxides may be taken as types :—

Manganous oxide, MnO.
Manganic oxide, Mn_2O_3.
Manganic anhydride, MnO_3.
Permanganic anhydride, Mn_2O_7.

Manganous oxide is a strong, and manganic oxide, a weak base. The two latter are anhydrides, and form corresponding series of acids and salts.

460. Manganous Chloride, $MnCl_2,4H_2O$.—During the manufacture of chlorine by the action of hydrochloric acid on manganese dioxide, MnO_2, large quantities of this body are obtained as a bye-product. The waste liquor is evaporated so as to drive off excess of acid, diluted with water, and precipitated manganous sulphide added in slight excess. This forms insoluble sulphides with any iron, cobalt, and nickel present, being itself transformed into the soluble chloride. The sulphides are filtered off, and the liquid evaporated, when crystals of the chloride are deposited. They are somewhat deliquescent and readily soluble in water, giving a neutral reaction to litmus. Manganous chloride has no tendency in the presence of air to oxidise to higher compounds.

Manganic Chloride, Mn_2Cl_6, is produced by treating the corresponding oxide, M_2O_3, with hydrochloric acid in the cold. It readily decomposes, with evolution of chlorine and the formation of manganous chloride.

Manganic Tetrachloride, $MnCl_4$, is even more unstable than Mn_2Cl_6; it is of interest as the corresponding chloride to the dioxide, and is momentarily formed in the preparation of chlorine from the dioxide and hydrochloric acid.

461. Manganous Oxide, MnO.—This body is produced by the ignition of manganous carbonate, $MnCO_3$, in the absence of oxygen. It is a greenish compound, which readily absorbs oxygen, being converted into a higher oxide. The corresponding hydrate, $Mn(HO)_2$, is formed when potassium hydrate is added to a soluble manganous salt; but through the absorption of oxygen from the air, an oxyhydrate is rapidly formed.

462. Manganic Oxide, Mn_2O_3.—This form of manganese oxide occurs in nature, and may also be prepared artificially by various methods, but is liable to be contaminated with other oxides.

Manganese Red Oxide, Mn_3O_4, or MnO,Mn_2O_3, may be viewed as a compound of manganous and manganic oxides, and so is analogous in composition to magnetic oxide of iron. It is formed when any other oxides of manganese are ignited in air, and is an indifferent body, yielding, when dissolved in cold concentrated sulphuric acid, a mixture of manganous and manganic sulphates.

463. Manganese Dioxide, MnO_2.—This is the most plentiful natural source of manganese, and at ordinary temperatures is perfectly stable; but when heated evolves oxygen, with the formation of the red oxide, Mn_3O_4. It is consequently employed as a source of free oxygen and an oxidising agent. As the corresponding chloride, $MnCl_4$, is most unstable, the action of manganese dioxide on hydrochloric acid is the principal source of chlorine. Dissolved in concentrated sulphuric acid it yields manganous sulphate and free oxygen :—

$$\underset{\text{Manganese dioxide.}}{2MnO_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Manganous sulphate.}}{2MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}.$$

464. Manganous Sulphate, $MnSO_4,5H_2O$. — This salt is prepared by heating purified manganese dioxide with concentrated sulphuric acid, igniting, to decompose ferrous

sulphate, and then lixiviating with water. On evaporation, pinkish crystals of the sulphate are deposited: these are not deliquescent but dissolve readily in water. The solution is used as a mordant in calico-printing.

Manganic Sulphate, $Mn_2(SO_4)_3$, does not crystallise, but, like iron and chromium, forms an alum with potassium sulphate, manganese alum, $K_2Mn_2(SO_4)_4,24H_2O$.

465. Other Salts of Manganese.—Among these may be mentioned the sulphide, MnS, obtained as a flesh-coloured precipitate on adding sulphuretted hydrogen to manganous sulphate in the presence of ammonia.

Manganous Carbonate, $MnCO_3$, is isomorphous with ferrous carbonate, and readily evolves its carbon dioxide on being heated.

466. Manganic Acid and Manganates.—Manganese trioxide, which may be regarded as the anhydride of manganic acid, may be obtained as an unstable amorphous mass, readily decomposed into permanganic acid, $HMnO_4$, and manganese dioxide, by the addition of water.

Potassium Manganate, K_2MnO_4, is formed by heating together manganese dioxide and caustic potash, in the presence of air or other oxidising agent; MnO_3 is formed and combines with potassium oxide to produce the manganate. On treating the fused mass in the cold with a small quantity of water a green solution is obtained, from which crystals of the manganate are formed by evaporation *in vacuo* over sulphuric acid. These are isomorphous with potassium chromate, K_2CrO_4. In solution, potassium manganate is most unstable, being decomposed by the addition of water into the following substances:—

$$\underset{\text{Potassium manganate.}}{3K_2MnO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Manganese dioxide.}}{MnO_2} + \underset{\text{Potassium hydrate.}}{4KHO} + \underset{\text{Potassium permanganate.}}{2KMnO_4}.$$

With this addition of water the colour changes through various shades of red to a magnificent purple tint, hence this body formerly received the name of mineral chameleon. The manganates readily evolve oxygen, and act as powerful

oxidising agents: they are in consequence largely used as disinfectants.

467. Permanganic Acid and Permanganates.—Manganese heptoxide, Mn_2O_7, may be viewed as the anhydride of permanganic acid. It may be prepared as a very unstable compound by dissolving potassium permanganate in cooled concentrated sulphuric acid, and then cautiously adding water. A brown liquid separates, consisting of the heptoxide; it is very unstable and spontaneously decomposes, even at low temperatures, with the evolution of oxygen; on the temperature being raised it suddenly and entirely decomposes, with violent explosion.

Potassium Permanganate, $KMnO_4$, is formed by the addition of water to a solution of the manganate, or still better by passing chlorine through the solution, when the following reaction occurs:—

$$\underset{\text{Potassium manganate.}}{2K_2MnO_4} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Potassium permanganate.}}{2KMnO_4} + \underset{\text{Potassium chloride.}}{2KCl.}$$

On concentration, acicular crystals of the permanganate, of a bluish-black colour, crystallise out. They are isomorphous with those of potassium perchlorate. On being heated the permanganate is decomposed, with the evolution of oxygen and production of caustic potash and manganese dioxide:—

$$\underset{\text{Potassium permanganate.}}{4KMnO_4} = \underset{\text{Potassium hydrate.}}{2K_2O} + \underset{\text{Manganese dioxide.}}{2MnO_2} + \underset{\text{Oxygen.}}{5O_2.}$$

The permanganates in solution produce a superb violet colour and are more stable than the manganates, although they contain a higher proportion of oxygen. In the laboratory, potassium permanganate is employed as an oxidising agent, and as such forms the basis of an interesting series of determinations in volumetric analysis. Thus, for example, in the presence of sulphuric acid, potassium permanganate oxidises ferrous to ferric sulphate in the following manner:—

$$\underset{\text{Potassium permanganate.}}{2KMnO_4} + \underset{\text{Ferrous sulphate.}}{10FeSO_4} + \underset{\text{Sulphuric acid.}}{8H_2SO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} +$$

$$\underset{\text{Manganous sulphate.}}{2MnSO_4} + \underset{\text{Ferric sulphate.}}{5Fe_2(SO_4)_3} + \underset{\text{Water.}}{8H_2O.}$$

An examination of this equation will show that the two molecules of potassium permanganate have yielded five atoms of oxygen for oxidising purposes. In performing the analysis, a permanganate solution is taken of known strength, the iron solution to be estimated is reduced completely to the ferrous state, and then permanganate run in until the violet tint of the salt in solution just remains permanent. The quantity of permanganate taken is the measure of the quantity of iron present. A solution of potassium dichromate is used in a similar manner.

Potassium permanganate is now used in large quantities as a disinfectant; it is odourless, and produces by oxidation odourless compounds. It is nevertheless an active destructive agent of germ life, and is consequently widely employed for this purpose. Condy's fluid is a solution of either potassium or sodium permanganate; the latter is prepared in the same manner but does not crystallise so readily as the potassium salt.

Permanganic Acid, $HMnO_4$, is prepared by adding dilute sulphuric acid to barium permanganate, $Ba(MnO_4)_2$. It is very unstable, readily decomposing on the application of heat, with evolution of oxygen.

Cobalt—Symbol, Co. Atomic weight, 58·6.

468. **Occurrence.**—Cobalt occurs as an arsenide, $CoAs_2$, known as speiss-cobalt, and also as sulphide. The compounds of this metal are not plentifully distributed, and are usually found in association with ores of nickel, iron, and manganese.

469. **Preparation and Properties.**—By igniting the oxalate in a porcelain crucible lined with lime, a fairly pure form of cobalt is obtained. This crucible should be enclosed in another of clay, and the space between filled with charcoal; they are then subjected to the most intense heat of a furnace for about two hours, when a button of cobalt remains. Cobalt is a metal which in appearance and properties closely resembles iron. It is harder, but melts at a lower temperature. Cobalt decomposes steam at a red heat, and is dissolved by hydrochloric and sulphuric acids, with evolution of hydrogen. This metal has received no important application in the arts.

470. Compounds of Cobalt.—There are two series of cobalt compounds, of which the following oxides may be taken as types. These are :—

Cobaltous oxide, CoO.
Cobaltic oxide, Co_2O_3.

The former is strongly, and the latter weakly basic.

471. Cobaltous Chloride, $CoCl_2$.—This salt is obtained by passing chlorine over metallic cobalt, and also by dissolving either the hydrate or carbonate in hydrochloric acid. The solution yields crystals represented by the formula $CoCl_2,6H_2O$, which are red in colour, deliquescent, and very soluble in water. On being gently heated the water is expelled and the anhydrous chloride, which is of a bright blue, is formed. A solution of cobaltous chloride may be used as ink, and leaves a scarcely visible pink mark. On warming the paper, so as to expel the water from the chloride, the writing becomes vividly blue. The blue again gradually fades with absorption of moisture from the atmosphere.

Cobaltic chloride, Co_2Cl_6, may be prepared by dissolving cobaltic oxide in hydrochloric acid; it is, however, very unstable, and on warming evolves chlorine, with the formation of the cobaltous salt.

472. Cobaltous Oxide, CoO.—This oxide may be prepared by igniting the carbonate, so arranging the vessel that the oxide cools in the atmosphere of evolved carbon dioxide, as otherwise it absorbs oxygen. At a red heat it forms the oxide Co_3O_4, corresponding to those produced by heating manganese and iron oxides. In the wet way the hydrate, $Co(HO_2)$, is precipitated by potassium hydrate from the nitrate or chloride. This, on being heated, yields the anhydrous oxide, but while wet readily absorbs oxygen from the air.

Cobaltous oxide combines with zinc oxide and other bases, yielding definite coloured compounds ; these are employed as pigments, and the reaction is of service in blowpipe analysis.

Cobaltic oxide, Co_2O_3, is a very weak base, and may be prepared by passing chlorine through water in which cobaltous

hydrate is suspended. In this way the black cobaltic hydrate, $Co_2(HO)_6$, is formed, from which the water may be expelled by moderately heating.

473. **Cobaltous Nitrate, $Co(NO_3)_2,6H_2O$.**—On dissolving the oxide in nitric acid and evaporating, red deliquescent crystals of this salt are formed. The nitrate is soluble in water, the solution being used as a blowpipe reagent.

474. **Silicates of Cobalt.**—In combination with silicate of potassium, cobalt silicate forms an important colouring matter known as smalt. This is prepared by first roasting cobalt ore and obtaining therefrom a crude cobalt oxide termed zaffre. From this iron and various other impurities are removed by solution and precipitation by sulphuretted hydrogen and other reagents. This cobalt oxide is mixed with siliceous sand and potassium carbonate, and heated in crucibles arranged in furnaces similar to those employed in glass-making. A deep blue glass is formed; this is ground under water to a fine powder, and yields a blue pigment, used by paper-stainers and others.

The salts of cobalt, like those of chromium, are distinguished by their well-marked colours.

475. **Other Salts of Cobalt.**—Among these the following may be briefly mentioned:—

Cobalt sulphides.—Of these the monosulphide, or cobaltous sulphide, CoS, is produced by adding sulphuretted hydrogen to a soluble cobaltous salt in the presence of ammonia. By heating cobaltic oxide, Co_2O_3, in sulphuretted hydrogen gas, the corresponding sulphide, Co_2S_3, is formed.

Cobaltous sulphate, $CoSO_4,7H_2O$, is isomorphous with that of iron.

Cobaltous carbonates are formed on adding sodium carbonate to a solution of the chloride; they are basic, and vary in composition according to the temperature at which precipitated.

Ammoniacal Salts of Cobalt.—Cobalt forms an extensive series of double salts with ammonia, for the preparation

and properties of which reference must be made to the larger treatises on chemistry.

Nickel.—Symbol, Ni. Atomic weight, 58·6.

476. **Occurrence.**—Nickel occurs in nature as the arsenide, Kupfernickel, NiAs, and also as a silicate. Nickel ores are, with very few exceptions, associated with those of cobalt; copper, iron, and manganese are also usually present as impurities. Cobalt and nickel not only resemble each other closely in appearance, but are in addition so alike in properties and general behaviour that their separation is a matter of some difficulty.

477. **Preparation.**—Nickel is obtained at Birmingham from its ores by the following series of processes. The ores are first roasted in reverberatory furnaces, so as to expel the arsenic, which condenses in coke-towers through which the furnace gases pass on their escape. The ore is next digested with hydrochloric acid, by which nickel, cobalt, iron, copper. arsenic, and other metallic impurities are dissolved. The solution is first treated with chloride of lime (bleaching powder), and in this manner the iron is precipitated as ferric oxide, and carries down with it the arsenic. After removal of the precipitate, sulphuretted hydrogen is passed, in order to throw down any copper, bismuth, and lead. A solution is thus obtained, containing practically only the cobalt and nickel; this is warmed and more bleaching powder added at the higher temperature; cobaltic oxide, Co_2O_3, is precipitated and removed by filtration. To the filtrate, milk of lime is added, and the nickel obtained as the hydrate, $Ni(HO)_2$. The hydrated oxide, on being heated with charcoal, is reduced at a white heat to metallic nickel, which finds its way into the market in small cubical ingots.

478. **Properties.**—Nickel is a silvery-white, hard metal. It fuses more readily than iron, than which it possesses more tenacity. Nickel does not oxidise in air so readily as does iron; but combines with oxygen at a high temperature, at a red heat also decomposing steam. Chlorine and bromine

readily attack the metal. Hydrochloric and sulphuric acids dissolve it, with evolution of hydrogen. Nickel is slightly magnetic, but possesses this property to a much less extent than iron.

479. **Industrial Applications.**—In conjunction with copper and zinc, nickel produces alloys which are characterised by their remarkably white appearance. These are known as German silver, packfong, and by other names; the material is used as an imitation silver for making spoons and other articles.

Owing to its hardness, capacity for taking a high polish, and freedom from tendency to become tarnished, nickel is now extensively employed in electro-plating parts of machines, knives, and other objects.

480. **Nickelous Chloride, $NiCl_2,9H_2O$.**—This chloride is formed by dissolving the oxide in hydrochloric acid, from which it is obtained as green crystals. Nickelous chloride is partly decomposed on being heated in air, with the formation of the oxide and liberation of chlorine. At high temperatures the chloride is volatile and may be sublimed.

481. **Nickelous Oxide, NiO.**—In the anhydrous condition, this compound may be obtained by heating the carbonate or nitrate. In the wet way, the hydrate, $Ni(HO)_2$, is formed by the addition of sodium hydrate to a solution of the sulphate, when a light green precipitate occurs. This is the only oxide which forms salts.

Nickelic oxide, Ni_2O_3, is produced in the hydrated condition, $Ni_2(HO)_6$, by adding sodium hypochlorite to nickelous hydrate suspended in water. On treatment with acids it evolves oxygen and forms nickelous salts.

482. **Nickelous Sulphate, $NiSO_4,7H_2O$.**—By dissolving either the carbonate or the metal in sulphuric acid and evaporating, rich green crystals of the sulphate are formed. These are isomorphous with those of iron, and soluble in water.

483. **Other Nickel Salts.**—Nickel forms several sulphides, among which there is nickelous sulphide, NiS, pro-

duced in the hydrated form when the sulphate is treated with hydric ammonium sulphide.

Nickel produces several basic carbonates by precipitation of its sulphate with sodium carbonate, but by pouring the sulphate into large excess of hydric sodium carbonate solution the normal carbonate, $NiCO_3$, is formed.

CHAPTER XXVI

TIN AND ARSENIC GROUP

Tin.—Symbol, Sn. Atomic weight, 117·8.

484. Occurrence.—Tin occurs native in the form of tin-stone or cassiterite, which substance is stannic oxide, SnO_2. The ore of this metal is not very widely distributed, its principal sources being the Cornish tin mines, and also those of Banca and Australia. Tinstone is found in veins or lodes in granitic and adjacent metamorphic rocks, and also as 'stream-tin' in the beds of rivers in tin-yielding districts.

485. Extraction.—The tin ore is first hand-picked, then crushed to a fine powder by the action of a series of heavy, falling weights called *stamps*; from these it is washed into pits and allowed to subside. The ore is next purified by repeated washing operations, in which the higher gravity of the tinstone serves the purpose of effecting its separation from the earthy matter present in the ore, which is washed away. Tin ore is next subjected to a roasting operation in order to expel arsenic and sulphur. The operation of reduction is effected by mixing the ore with about one-fifth its weight of anthracite coal and a little lime, heating first gently and afterwards more strongly for about six hours, when the reduced tin is run out into iron pans. It next undergoes a process of purification termed *liquation*, the tin being heated sufficiently to partly melt it. The purer tin melts first, and leaves behind an impure alloy with iron and other metals, with a higher melting-point. A

further process of purification consists of melting the metal in iron pans and then stirring with wet wood-stakes; the agitation caused by the rising steam causes the separation of the slag and other impurities. The purified tin is cast into ingots.

486. Properties.—Tin is a lustrous white metal, somewhat harder than lead. It is malleable and may readily be reduced to thin sheets, sold as tinfoil. Near its melting-point tin is brittle, and if dropped from a height breaks in pieces; at a very low temperature also (freezing-point of mercury) tin becomes brittle and falls into a coarse powder. Tin on being bent emits a peculiar grinding sound, caused by the internal friction of its crystal surfaces. The metal melts at 227° C., and volatilises at about 1500°. Tin only slowly tarnishes on exposure to air at ordinary temperatures, but burns when strongly heated. It decomposes water at a red heat, with evolution of hydrogen. Hydrochloric acid dissolves tin, with evolution of hydrogen; sulphuric acid and nitric acid also attack the metal, with the formation of compounds to be subsequently described. Sulphur, bromine, and chlorine all unite directly with tin.

487. Industrial Applications. Among these, the most important is that of making tin-plate. This well-known material consists of sheets of pure iron, cleaned and then alloyed with tin on the surface. Tin is also used in conjunction with copper to form the alloy known as bronze. A number of alloys of tin with other metals are employed for various purposes. An amalgam of tin and mercury is employed as the reflecting coating of glass mirrors.

488. Compounds of Tin.—Tin forms two series of salts, known respectively as stannous and stannic compounds. Stannic oxide in the hydrated condition possesses acid properties, and with strong bases yields salts called stannates.

489. Stannous Chloride, $SnCl_2,2H_2O$.—This salt may be prepared by heating tin in a current of hydrochloric acid gas; it fuses at 250° and boils at 606°. The vapour at low temperatures has a density less than is required by the formula,

Sn_2Cl_4, but at a greater heat agrees closely with $SnCl_2$. In the wet way, stannous chloride is formed by dissolving granulated tin in concentrated hydrochloric acid, with the aid of a gentle application of heat. The operation is usually conducted in copper vessels, as the two metals in contact induce voltaic currents which result in the more rapid solution of the tin. The liquid on being concentrated deposits crystals containing two molecules of water. Stannous chloride is soluble in a small amount of water, but on the addition of a greater quantity is thrown down as a precipitate of stannous oxychloride, $SnCl_2,SnO,2H_2O$. Owing to the great readiness with which stannous chloride combines both with chlorine and oxygen, it is a powerful reducing agent. It is used in both dyeing and calico-printing as a mordant, being known under the name of tin-salts.

490. **Stannic Chloride, $SnCl_4$.**—This salt is formed by direct combination of dry chlorine with melted tin. In the pure state it is a thin colourless liquid, which boils at 113·9°. It may also be produced by dissolving tin in aqua regia, or in an impure form by employing a mixture of nitric acid and ammonium chloride as the solvent. The anhydrous salt fumes on exposure to air, and readily combines with water to form a hydrate, which is a semi-solid substance known sometimes as 'butter of tin'; in small quantities of water it is freely soluble, but larger quantities effect its decomposition, with precipitation of hydrated stannic oxide. The salt is readily held in solution by hydrochloric acid, and is employed as a mordant in dyeing.

491. **Stannous Oxide, SnO.**—This compound may be obtained in the hydrated form, $Sn(HO)_2$, by the addition of sodium carbonate to a solution of stannous chloride. By careful ignition in an indifferent atmosphere, either of nitrogen or carbon dioxide, it may be rendered anhydrous. Stannous oxide readily combines with oxygen and is converted into stannic oxide.

492. **Stannic Oxide, SnO_2.**—Cassiterite, or tinstone, is a native form of this oxide, which in the pure crystalline form is transparent and colourless. Acids are without action on

the native oxide, which, however, is attacked by the alkalies, forming soluble compounds termed stannates.

Metastannic Acid, $H_2Sn_5O_{11},4H_2O$, is produced by the action of tin on moderately concentrated nitric acid; nitrous fumes are evolved, ammonium compounds formed, and a white crystalline mass deposited, which on being washed and gently dried has the above composition. This body is acid to litmus-paper, and on being heated loses its water and is changed into anhydrous stannic oxide, which prepared in this manner is known as putty powder. Metastannic acid dissolves in sodium or potassium hydrate solution, and forms soluble metastannates, which are not susceptible of crystallisation.

Stannic Acid, H_2SnO_3, is formed by the addition of calcium carbonate to stannic chloride in slight excess. A gelatinous precipitate of the acid is formed, which after thorough washing reddens litmus. The acid dissolves in the hydrates of sodium and potassium, forming the respective salts. Sodium stannate is prepared for industrial purposes by fusing tinstone with caustic soda and lixiviating the fused mass; the salt crystallises out on concentration of the solution. Like several others of the tin compounds, it is employed in calico-printing, and is known as 'tin-prepare liquor.'

493. **Tin Sulphides.**—These correspond to the oxides, and, in addition, there is a sesquisulphide, $Sn\,S_3$.

Stannous Sulphide, SnS, is formed when tin and sulphur are heated together, or when tin is melted in an atmosphere of sulphuretted hydrogen. In the hydrated form stannous sulphide is precipitated by sulphuretted hydrogen from solutions of stannous salts.

Stannic Sulphide, SnS_2, is a substance of some industrial importance, being known as mosaic gold, and employed as a bronzing powder. It is prepared by heating together an amalgam of tin and mercury, sulphur, and ammonium chloride. Mercurous chloride and mercuric sulphide sublime, and leave behind a mass of scaly yellow, gold-like crystals, which are only attacked among the acids by aqua regia, but are dissolved by the caustic alkalies.

494. **Other Salts of Tin.**—Tin forms a sulphate, $Sn(SO_4)_2$, soluble in dilute sulphuric acid, but precipitated by the addition of water. Bromides and iodides may be prepared by methods analogous to those used for forming the chlorides, to which bodies they bear a general resemblance.

Arsenic.—Symbol, As. Atomic weight, 74·9. Observed density, 152·96. Molecular weight, 299·6.

495. **Occurrence.**—Arsenic is at times found in the free state in nature, but more frequently in combination with iron and other metals. Its most common ore is mispickel, an arsenical iron pyrites, FeAsS, found in Cornwall and also in Silesia.

496. **Preparation.**—Metallic arsenic is prepared by reducing its oxide, As_4O_6, by heating with charcoal in a crucible having another inverted on the top as a lid. The arsenic sublimes and condenses on the interior of the relatively cool upper crucible.

497. **Properties.**—Arsenic has a greyish colour, and metallic lustre. The metal is very brittle, and sublimes at ordinary atmospheric pressures without melting, but fuses when heated under pressure. Arsenic, like phosphorus, forms a tetratomic molecule, which at very high temperatures is dissociated into two diatomic molecules. On condensing from sublimation, crystals are formed which are isomorphous with those of antimony. Arsenic is a good conductor of electricity. During its sublimation a characteristic garlic-like odour is observed; the vapour is of a light yellow colour. At ordinary temperatures the dry metal is unaffected by air, but on being heated burns with the formation of the oxide, As_4O_6. Nitric acid attacks the metal, with the formation of arsenic acid. Arsenic and most of its soluble compounds are intensely poisonous. In the metallic form this metal is employed in the manufacture of shot, as its alloy with lead more readily assumes the globular form than does the latter metal when used alone.

498. **Compounds of Arsenic.**—The anomalous position occupied by this element has been already referred to. On

the one hand it exhibits similarities with nitrogen and phosphorus, and on the other is closely related to antimony and bismuth. In the elementary form, arsenic may fairly lay claim to be considered a metal, having, in a well-marked degree the physical characters associated with that class of bodies. But it is distinguished from the metals proper by forming no salts with oxy-acids. Thus, with nitric acid it forms not an arsenic nitrate, but arsenic acid. In this respect, however, it resembles tin, which produces, under similar circumstances, metastannic acid. In common with antimony, arsenic forms two oxides, which both produce acids and salts. Antimony, however, does in one or two instances act as a base, and so is definitely included among the metals. Possibly, were a lower oxide of arsenic to be discovered than As_4O_6, it would be found to be basic in character, and to form salts in which it would fulfil basic functions.

499. **Arsenic Hydride, or Arseniuretted Hydrogen, AsH_3.**—In common with phosphorus and nitrogen, arsenic forms a gaseous compound, with hydrogen.

Preparation.—This gas is obtained in the pure state by treating zinc arsenide with dilute sulphuric acid—

$$\underset{\text{Zinc arsenide.}}{As_2Zn_3} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} = \underset{\text{Zinc sulphide.}}{3ZnSO_4} + \underset{\text{Arseniuretted hydrogen.}}{2AsH_3}.$$

Mixed with large excess of hydrogen, it is readily obtained by introducing an arsenious compound into the apparatus in which hydrogen is being evolved from zinc and dilute sulphuric acid.

Properties.—Arseniuretted hydrogen is a colourless gas, with a most offensive and disagreeable garlic-like odour. **It is one of the most poisonous substances known, and therefore requires the greatest care in all experiments in which it is used.** Arsenic hydride may be condensed to a colourless liquid by subjection to a temperature of $-30°$ C. The gas is only very sparingly soluble in water, and exhibits no alkaline properties, differing in this respect from ammonia, which is strongly alkaline, and phosphoretted hydrogen, which in a few instances behaves in a manner similar to ammonia,

as in the formation of phosphonium iodide, PH_4I. Arseniuretted hydrogen is inflammable, burning with a lurid blue flame, and forming arsenious oxide and water. If burned with a limited supply of air, or if the flame be suddenly cooled, the hydrogen only enters into combination with oxygen, and the arsenic is deposited in the elementary form. The gas is decomposed by being passed through a red-hot tube, when a crust, or 'mirror,' of free arsenic is deposited beyond the heated spot.

500. **Arsenious Chloride, $AsCl_3$.**—Metallic arsenic takes fire spotaneously when dropped into chlorine gas, forming this, the only chloride. It is an oily-looking liquid, which fumes on exposure to air, and is converted by water into hydrochloric and arsenious acids.

501. **Arsenic Sulphides.**—Several of these are known, the most important being realgar, As_2S_2; arsenious sulphide, As_2S_3; and arsenic sulphide, As_2S_5.

Realgar occurs native in ruby-red crystals, and may be prepared by fusing together nine parts of metallic arsenic and four of sulphur. In this way an amorphous glassy mass is formed, having a bright red colour. Realgar is attacked by nitric acid or aqua regia, forming arsenic acid, with a separation of free sulphur, which latter is slowly dissolved by prolonged treatment with the acid. Realgar, when mixed with nitre and sulphur, deflagrates with an exceedingly bright light.

Arsenious Sulphide, or orpiment, As_2S_3, is deposited as a golden-yellow precipitate when sulphuretted hydrogen is passed through a solution of arsenious acid in hydrochloric acid. It burns with a pale flame on being heated in air, but in closed vessels may be sublimed. Commercial orpiment is prepared by subliming together seven parts of arsenious oxide with one of sulphur. Thus prepared, it yields a yellow, vitreous mass, containing uncombined arsenious oxide in considerable quantity. This sulphide is insoluble in dilute acids, slowly attacked by nitric acid, but easily dissolved by ammonia and the alkalies. Orpiment, finely ground, constitutes the pigment termed King's yellow.

Arsenic Sulphide, As_2S_5, may be formed by fusing together arsenious sulphide with the proper proportion of sulphur.

502. **Arsenious Oxide, or Arsenious Anhydride, As_4O_6.—Observed vapour-density, 199·85. Molecular weight, 395·4.**—This body is that known to the public as arsenic, and commercially as white arsenic; it is the form in which arsenic is first extracted from its ores.

Manufacture.—Arsenical pyrites are mixed with a small quantity of smokeless coal (anthracite) and roasted in a reverberatory furnace; the double arsenide and sulphide are decomposed, with the formation of arsenious oxide and sulphur dioxide. The products of combustion are led through a series of chambers, in which the white arsenic is deposited, the sulphur dioxide escaping into the air.

Properties.—As thus obtained, arsenic occurs as either a coarse crystalline powder, or in vitreous masses. These latter are at first transparent, but gradually become opaque and porcelain-like on keeping. Arsenious oxide is without odour, and has a faint, sweet, metallic taste. It sublimes without fusion, and its vapour corresponds with the formula As_4O_6, which is double that of the oxide of nitrogen. The formula is more commonly written As_2O_3, and the substance is very frequently termed arsenic trioxide. Arsenious oxide is feebly soluble in water, and more readily soluble in hydrochloric acid. By nitric acid it is converted into arsenic acid. White arsenic is an exceedingly poisonous body.

Industrial Applications.—Arsenious oxide forms the starting-point in the manufacture of other arsenic compounds. It is employed in the preparation of a number of pigments, and also in the manufacture of glass. In this latter case it acts as an oxidising agent, converting the ferrous oxide present into ferric oxide, and thus ridding the glass of its green tint.

503. **Arsenious Acid, H_3AsO_3.**—Arsenious oxide, dissolved in water, produces a liquid having an acid reaction, but the pure acid has not been freed from excess of water. It

forms, however, a number of salts called arsenites, which in composition agree more or less with the phosphites. It will be remembered that these compounds have the general formula M'_2PHO_3, but that normal tribasic phosphites, M'_3PO_3, can be formed. Arsenious acid produces arsenites of the formula M'_2HAsO_3, but also forms more readily than does the corresponding phosphorous acid, normal tribasic salts.

Potassium Arsenite, K_3AsO_3, is formed by dissolving arsenious oxide in a solution of potassium carbonate, and is known in medicine as Fowler's solution.

Hydric Cupric Arsenite, $CuHAsO_3$, is known as Scheele's green, and is a pigment of a beautiful green colour. Owing to its excessively poisonous nature its employment is to be altogether condemned.

From the readiness with which arsenious oxide combines with oxygen, arsenious acid and the arsenites constitute powerful reducing agents.

504. Arsenic Oxide or Anhydride, As_2O_5, and Acids.—On gently heating together arsenious oxide and nitric acid, the former is oxidised to arsenic acid.

$$\underset{\text{Arsenious oxide.}}{As_2O_3} + \underset{\text{Nitric acid.}}{2HNO_3} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Arsenic acid.}}{2H_3AsO_4} + \underset{\text{Nitrogen trioxide.}}{N_2O_3}.$$

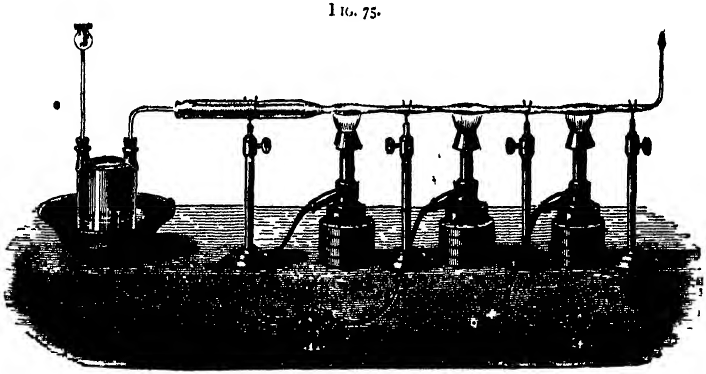
As this solution cools it deposits crystals of a hydrate of arsenic acid, having the formula $2H_3AsO_4.H_2O$. At a temperature of 100° C. these crystals lose the molecule of water of crystallisation, and ortho-arsenic acid, H_3AsO_4, is formed. At a higher temperature, 180°, two molecules of the acid coalesce and lose another molecule of water, yielding pyr-arsenic acid, $H_4As_2O_7$. On being subjected to further heat this is converted into met-arsenic acid, $HAsO_3$. It will be seen from this that the arsenic acids correspond to the analogous series of phosphoric acids. On the addition of water, pyr- and met-arsenic acids are at once converted into the ortho- variety. The application of further heat to met-arsenic acid results in the production of arsenic oxide as a white deliquescent mass. Arsenic acid is a powerful acid, dissolving the alkaline carbonates with effervescence.

Industrial Applications.—Arsenic acid is used in calico-printing, and also largely in the manufacture of magenta dye from aniline.

Arsenates.—These are isomorphous with the corresponding phosphates: thus, there are three sodium arsenates in which the hydrogen is replaced atom by atom from the acid. The arsenates of the alkalies are soluble, but the others are insoluble in water, but soluble in dilute nitric acid. With any soluble arsenate, argentic nitrate precipitates silver arsenate, Ag_3AsO_4, of a characteristic brick-red tint. Like arsenic acid, sodium arsenate, Na_2HAsO_4 is used in calico-printing.

505. **Detection of Arsenic.**—The analytic detection of substances generally is not included within the scope of this

FIG. 75.



work; but as one test at least involves some interesting chemical properties of arsenic, it will be here described. The test referred to is that known as Marsh's test, and depends on the fact that arseniuretted hydrogen is evolved when arsenious bodies are introduced into a zinc-evolving apparatus. For this purpose, the apparatus shown in fig. 75 is fitted up. This consists, in the first place, of a Woulffe's bottle fitted with thistle-funnel and delivery tube. To this is attached a piece of combustion-tubing, drawn out in the manner shown in the engraving. The end nearest the Woulffe's bottle is packed with

cotton-wool, so as to retain any splashes of liquid. The drawn-out tube is heated in several places by bunsen-burners. To commence the test pure zinc is placed in the Woulffe's bottle, and on it is poured a mixture of sulphuric acid, one part to eight parts of water. Hydrogen gas is evolved, and after this has expelled the whole of the air from the apparatus, the bunsen-burners are lighted, and the current of hydrogen maintained for some minutes. If the zinc and acid be pure there should not be the slightest stain in the interior of the combustion-tubing; but if any arsenic be present 'mirrors' will be formed within the tube. Supposing the reagents are thus proved to be free from arsenic, the suspected liquid is added, a few drops at a time, through the thistle funnel; if any arseniuretted hydrogen be found it is decomposed by the heat of the burners, and a brown or black mirror of arsenic is deposited. As antimoniuretted hydrogen produces the same effect, yielding a mirror of antimony, it is necessary to be able to distinguish the one from the other. This may be effected in various ways, thus the mirrors may be treated with a solution of sodium hypochlorite; this dissolves the arsenic mirror almost immediately, but acts very slowly on antimony. Another very good method is to oxidise the mirror by heating the enclosed tube containing it. Its ends being open, the current of air which passes through converts the metal into oxide. On next passing sulphuretted hydrogen gas through the tube the oxide is changed to sulphide, and each, whether it be arsenious or antimonious sulphide, is known by its colour.

Antimony.—Symbol, Sb. Atomic weight, 122.

506. Occurrence.—Antimony occurs somewhat abundantly, and is usually obtained from its sulphide, Sb_2S_3, which substance is known as antimonite.

507. Preparation.—Antimonite is one of the most easily fused minerals known; as a first step toward the preparation of the metal, the crude ore is heated, when the antimonite melts, and is thus separated from the gangue or earthy impurities. This fused sulphide constitutes the crude antimony of commerce. To obtain metallic antimony this substance is

roasted, so as to convert a portion of the sulphide into oxide, and reduced by heating with charcoal, when metallic antimony separates. The sulphide is also sometimes reduced by the action of metallic iron, which is converted into a sulphide on the separation of free antimony.

508. Properties.—Antimony is a metal of bluish-white colour, which is very brilliant and crystalline in structure, its crystals being isomorphous with those of arsenic. At a temperature of 450° the metal fuses, and boils at 1450°, but emits sufficient vapour at a lower temperature to permit of its density being measured. This, according to Meyer, is 178·9, which figure gives a molecular weight of 357·8. This does not agree with a tetratomic molecule, such as that of phosphorus or arsenic, but only slightly differs from the figures required for a triatomic molecule. If heated in contact with air, antimony burns with the formation of antimonious oxide. The molten metal in solidifying expands considerably, which property it also confers on its alloys. Concentrated hydrochloric acid dissolves antimony with evolution of hydrogen. Nitric acid oxidises it to antimonic oxide, Sb_2O_5. The metal combines readily with the halogens, taking fire spontaneously when thrown into chlorine.

509. Industrial Applications.—Antimony is employed in the manufacture of alloys, of which type-metal is one of the most important. The antimony not only enhances the hardness of the alloy, but also by its property of expanding at the moment of solidification produces a clean and sharp casting. Type-metal is composed of lead, tin, and antimony.

510. Compounds of Antimony.—These bear considerable resemblance to those of arsenic. Three oxides of antimony are known: antimonious oxide, Sb_2O_3, antimonic oxide, Sb_2O_5, and an intermediate oxide, Sb_2O_4. Of these bodies, the highest oxide possesses marked acid properties. The lowest acts as a weak acid, but also functions as a weak base.

511. Antimoniuretted Hydrogen, SbH_3.—By the introduction of soluble antimony compounds into a hydrogen-

evolving apparatus this gas is produced, although not so readily as is arseniuretted hydrogen. It is, when prepared in this manner, always associated with free hydrogen; unless thus diluted with hydrogen, the gas suffers spontaneous decomposition at ordinary temperatures, with the deposition of metallic antimony. It is a colourless gas, with a disagreeable odour and taste, and burns with the formation of water and antimonious oxide. It deposits a mirror of antimony when heated, in the same way as does arseniuretted hydrogen. The distinction between the two has already been explained.

512. Antimonious Chloride, $SbCl_3$.—This salt may be prepared in the dry way by passing chlorine over excess of antimony, or by heating together antimonious sulphate and sodium chloride, when sodium sulphate remains and antimonious chloride distils over. The salt may also be obtained by dissolving either antimony or antimonious sulphide in strong hydrochloric acid, and distilling the residual liquid. Antimonious chloride is a soft deliquescent substance, and hence has received the name of butter of antimony. It boils at 235° C., yielding a vapour whose density is 112·5. Antimonious chloride is soluble in a very small quantity of water, but on the addition of a large excess throws down a white oxy-chloride, SbOCl, formerly known as powder of Algaroth. This redissolves on addition of hydrochloric acid. Antimonious chloride is used as a coating for gun-barrels, which it thus browns and protects from rust.

Antimonic Chloride, $SbCl_5$, is formed by passing chlorine through gently warmed antimonious chloride. It is more volatile than the antimonious salt, and readily splits up into the tri-chloride, $SbCl_3$, and free chlorine.

513. Antimonious Oxide, Sb_2O_3.—This compound may be formed by boiling together antimony and concentrated sulphuric acid; the sulphate is formed, and this, on being treated with sodium carbonate, yields the oxide, which is isomorphous with the two forms in which arsenious oxide can be caused to crystallise. Antimonious oxide burns readily, with the formation of the higher oxide, Sb_2O_4. To strong

acids, as sulphuric acid, this oxide acts as a weak base ; to strong bases it behaves as a very weak acid, forming antimonites, to which reference will subsequently be made.

514. Antimonious Oxy-salts.—Either the metal or oxide is dissolved by concentrated sulphuric acid, on heating, with the formation of the sulphate, $Sb_2(SO_4)_3$. This is decomposed by water, with the formation of an acid and a basic salt.

An interesting property of antimonious oxide is that it readily dissolves in the comparatively weak organic acid, tartaric acid, or in a solution of its acid potassium salt, $KHC_4H_4O_6$. On boiling together this salt and antimonious chloride, and allowing the solution to cool, antimonyl potassium tartrate, or 'tartar emetic,' crystallises out. This body has the composition $K(SbO)C_4H_4O_6$, from which it will be seen that an atom of 'acid' hydrogen is replaced by the group SbO.

515. Antimonious Sulphide, Sb_2S_3.—This substance constitutes the native mineral antimonite, which has a metallic lustre, and somewhat resembles metallic arsenic in appearance. On roasting, the sulphide is partly converted into oxide ; the fused mixture of the two constitutes the antimony glass of commerce. On passing sulphuretted hydrogen through a solution of antimonious chloride, this sulphide is thrown down as an orange-coloured precipitate. Antimonious sulphide is soluble in a solution of sulphides of the alkalies, and is regarded as thus forming sulphantimonites in which sulphur replaces the oxygen of the corresponding oxy-acid. Antimonious sulphide is used in the mixtures employed for making the heads of lucifer matches, and also in the preparation of fireworks.

Antimonic Sulphide, Sb_2S_5, is precipitated when sulphuretted hydrogen is passed through an acid solution of the pentachloride, $SbCl_5$. It dissolves with extreme readiness in solution of the sulphides of the alkali metals. Sodium sulphide thus forms sodium sulphantimoniate, $Na_3SbS_4,9H_2O$, a salt whose formula (apart from the water of crystallisation) corresponds with that of sodium antimoniate, Na_3SbO_4.

516. Antimonites.—From a solution of potassium sulphantimonite, it is possible to obtain a substance having the composition $(HSbO_2)_2$, $8H_2O$. This is viewed as antimonious acid, and the corresponding sodium salt, $NaSbO_2$, has been prepared. This body, it will be noticed, is a metantimonious salt, and is the only normal salt of the acid as yet obtained in the crystallised form. Its existence serves to show the slight acid properties of antimonious acid.

517. Antimonic Oxide, or Anhydrite, Sb_2O_5.—Nitric acid acts violently on metallic antimony, and on gently heating the compound thus formed, Sb_2O_5 is obtained, a pale yellow powder almost insoluble in water, but which when moistened reddens litmus. Antimonic oxide dissolves in potassium hydrate solution, and thus forms potassium antimoniate, $KSbO_3$. On adding sulphuric acid to this solution, a hydrate of antimonic acid, $HSbO_3$, $2H_2O$, is precipitated as a white powder. Potassium antimoniate may also be prepared by heating antimony with potassium nitrate, and digesting the mass with warm water. In accordance with the nomenclature employed in describing the other members of this group of allied compounds, this acid and its salts should be termed metantimonic acid and metantimoniates. Custom has, however, given them the former name.

Metantimonic Acid, $H_4Sb_2O_7$, should properly be termed pyrantimonic acid; it is more especially of interest because it forms a soluble potassium metantimoniate, $K_4Sb_2O_7$, and an insoluble sodium metantimoniate, $Na_4Sb_2O_7$. In consequence, this is almost the only body which can be used as a precipitant for sodium compounds.

518. Other Antimony Compounds.—Antimony combines with the other members of the halogen group, forming bodies which bear a general resemblance to the chloride.

Also a tetroxide is known, possessing the formula, Sb_2O_4, which results from the application of heat to the pentoxide, Sb_2O_5. This body combines with potassium to form what has been called potassium hypoantimoniate, $K_2Sb_2O_5$.

Bismuth.—Symbol, Bi. Atomic weight, 210.

519. **Occurrence.**—Bismuth is mostly found in Saxony and Bohemia. It usually occurs in the free state, associated with cobalt and other ores.

520. **Extraction.**—Bismuth is obtained from its ores by the simple process of heating them in inclined iron tubes, when the metal drains off in the liquid state. As thus extracted, bismuth is not quite pure, but may be prepared in the pure state by precipitating the nitrate with excess of water, filtering, washing, drying, and igniting the residue with charcoal, by which it is reduced to the metallic state.

521. **Properties.**— Bismuth is a hard metal, with a reddish-grey colour. It may be easily powdered under the hammer, but is not so brittle as antimony, as it shows signs of being slightly flattened before entirely losing its coherence. It fuses at 268·3° C., and in solidifying expands considerably. Bismuth is distinguished by the readiness with which it assumes the crystalline form when solidifying from fusion. Its crystals are rhombohedrons, approaching very closely in shape to the cube. When heated bismuth is oxidised, and the metal decomposes steam at a red heat. It combines directly with chlorine, and also forms compounds with the other halogens. Hydrochloric acid is without action on the metal; sulphuric acid, when heated with it, forms a sulphate, with evolution of sulphur dioxide; nitric acid dissolves it readily with the formation of bismuthous nitrate.

522. **Industrial Applications.**—The principal use to which metallic bismuth is subjected is the preparation of what are termed fusible alloys. These possess the property, to a remarkable extent, of fusing below the melting-point of any of their constituents. Thus an alloy of four parts bismuth, two of lead, and one each of tin and cadmium, melts at 60·5° C. At the moment of solidification these alloys considerably expand. They are used for taking casts of engravers' blocks, and also for forming safety-plugs for steam-boilers and automatic fire-extinguishers. The composition of the alloy is so adjusted that in the boiler plug it melts if the water be allowed

to descend sufficiently low to expose the crown of the boiler tube to the action of the fire without being covered by water. In the fire-extinguisher a valve is arranged at the top of a room and soldered in its place by some of this alloy. An undue elevation of temperature fuses the plug, and at once the whole of the space within reach of the valve is flooded with water.

523. **Bismuthous Chloride, $BiCl_3$**, is obtained by heating bismuth in a current of chlorine, or by dissolving the oxide in strong hydrochloric acid and distilling. Bismuthous chloride is deliquescent, and dissolves in a small quantity of water, but with a larger quantity is precipitated as an oxychloride, BiOCl, known as 'pearl white.'

524. **Bismuthous Oxide, Bi_2O_3.**—This substance is obtained as a yellow powder by heating the nitrate or carbonate. It is insoluble in water, and is precipitated as a white hydrate, $Bi(HO)_3$, on adding ammonia to a solution of a bismuth salt. In properties it is feebly basic.

Bismuthic Oxide, Bi_2O_5, is obtained by heating bismuthic acid, $HBiO_3$. Bismuthic acid, and a metabismuthic acid, $H_4Bi_2O_7$, are known. They, however, form salts with great difficulty, about which very little is known.

525. **Bismuthous Sulphide, Bi_2S_3.**—This body occurs native, and is isomorphous with the corresponding antimony compound. In the dry way this body is formed when sulphur and bismuth are fused together. It is also produced as a black precipitate when sulphuretted hydrogen is passed through a solution of a bismuthous salt.

526. **Bismuthous Nitrate, $Bi(NO_3)_3, 5H_2O$.**—Bismuth differs from the other metals of this group in that it forms a nitrate when treated with nitric acid. From an acid solution this nitrate separates in colourless, prismatic, deliquescent crystals. These are soluble in a small quantity of water, but an insoluble basic nitrate is precipitated when water is added in large quantity.

527. **Other Compounds of Bismuth.**—These include compounds with the halogens, resembling in constitution the

chloride. Phosphates, chromates, and other salts of bismuth are also known; the latter is a crystalline powder of a fine yellow colour. A basic carbonate is formed on the addition of ammonium carbonate to a solution of the nitrate.

528. Characteristics of the Nitrogen-Bismuth Group.—These constitute an interesting group of elements. In the first place they fall into one of the families resulting from classification according to the periodic law. Starting with nitrogen, the atomic weight rises, and other properties undergo gradual changes, as shown in the following table :—

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic weight . . .	14·01	30·96	74·9	122·0	210·0
Metallic or non-metallic .	Non-metallic	Non-metallic	As element, metallic character; in compounds, non-metallic	Metallic as element, in compounds, only very slightly metallic in character.	Metallic
AH_3	Strongly basic.	Very slightly basic	Indifferent	Indifferent	Non-existent.
Nitric acid produces .	—	Phosphoric acid	Arsenic acid	Antimonic acid	Bismuth nitrate
A_2O_3 or A_4O_6 . .	Acid	Acid	Acid	Weakly acid and basic	Basic
A_2O_5	Strongly acid	Strongly acid	Acid	Moderately acid	Very weakly acid

In this table the symbol 'A' is used to signify an atom of either of the elements: thus A_2O_3 represents the trioxide of any number of the group. It will be seen that the chemical activity diminishes as the atomic weight increases. So does the metallic character, which physically is almost equally marked in arsenic and antimony; the former, however, have no basic compounds proper, while although the latter does form one or two oxy-salts, its more ordinary deportment, when oxidised, is as an acid. Bismuth does not form strong bases, but still the trioxide is decidedly basic; the higher oxide seems still to retain a vestige of acid properties.

CHAPTER XXVII

COPPER AND LEAD

Copper.—Symbol, Cu. Atomic weight, 63·0.

529. **Occurrence.**—Large quantities of copper occur in the native state. Among these the deposits of Lake Superior are worthy of special notice, as metallic copper is there found in massive veins some two feet in thickness. This copper is almost chemically pure. Copper also occurs in nature as red copper ore, or cuprite, Cu_2O, as basic carbonate in malachite and azurite, ores especially found in Russia and Australia; and as both the sulphide, chalcocite, Cu_2S, and the double sulphide, chalcopyrite, $CuFeS_2$. This latter constitutes the principal British ore of copper, being found in large quantities in Cornwall.

530. **Extraction.**—Copper is obtained from the oxide and carbonate varieties of ore by simply roasting the latter, by which it is converted into oxide, and then reducing by heating with carbon. The ores containing sulphur are in theory reduced by almost as simple a reaction. They are roasted so as to convert a part of the ore into oxide, and then heated in a reverberatory furnace in order to effect the following reaction :—

$$\underset{\text{Copper sulphide.}}{CuS} + \underset{\text{Copper oxide.}}{2CuO} = \underset{\text{Copper.}}{3Cu} + \underset{\text{Sulphur dioxide.}}{SO_2}.$$

In practice, however, this very simple reaction is attained by very complicated processes. In the first place, the ores requiring treatment vary considerably in composition, hence oxides and sulphides are mixed, so as to favour their simultaneous reduction in the manner shown, and then worked according to the methods which experience shows to be most suitable. Provision has also to be made in copper smelting processes for the removal of the iron ; this is usually effected by its transformation into a slag of iron silicate. The operations

of roasting and melting, with separation of slag, are repeated two or three times, resulting in each case in a 'regulus' or 'matt' richer in copper. In a final melting crude copper is obtained, which is refined by a process termed 'poling.' This consists in stirring the molten metal with poles of green wood. The gases evolved by the heat reduce the oxide of copper, which, dissolved in the metal, impairs its tenacity and other working qualities. For detailed descriptions of copper smelting, works on metallurgy must be consulted.

Considerable quantities of very poor copper ores are treated in the wet way, after first roasting with common salt; this converts the copper into a soluble chloride, which is precipitated in the metallic state by the action of scrap iron, ferrous chloride being formed.

531. **Properties.**—Copper is a moderately hard metal, of a red tint, susceptible of a high polish, and capable of retaining its lustre indefinitely in pure air. Copper possesses great tenacity and malleability, hence it may be drawn into wire, and hammered into very thin foil. Copper melts at about 1090° C., and is volatilised at the temperature of the voltaic arc. At a red heat copper combines readily with oxygen, but is unable to decompose water at any temperature. Copper and sulphur enter vigorously into combination when heated together, and the polished metal tarnishes quickly on exposure to sulphuretted hydrogen. Copper readily combines with chlorine, taking fire spontaneously when exposed in foil to the action of the gas. Neither pure water nor the presence of moisture in the air affects copper; sea-water and other solutions of chlorides attack the metal, with the formation of oxychloride of copper. Hydrochloric acid attacks copper with extreme slowness; concentrated sulphuric acid dissolves it on application of heat, with evolution of sulphur dioxide. Nitric acid violently attacks this metal, with evolution of nitrous fumes and formation of the nitrate. The metal slowly dissolves in ammonia. Pure copper is, second to silver, the best conductor of electricity known; it is also one of the best conductors of heat.

532. Industrial Applications.—Copper is a most widely used metal, being employed for those purposes in which great tenacity, combined with resistance to chemical action, is required, as in copper sheathing for wooden ships, the manufacture of boiler tubes, and other purposes. Copper wire and rope is extensively employed in the construction of electric conductors and cables. Copper is principally used in the manufacture of alloys, of which brass, an alloy of copper and zinc, and bronze, composed of copper, tin, and zinc, are the most important.

533. Cuprous Chloride, Cu_2Cl_2.—This compound is obtained by digesting cupric chloride with hydrochloric acid and metallic copper; the solution is filtered and poured into water, when a white precipitate of cuprous chloride is formed. This chloride is insoluble in water, but dissolves in hydrochloric acid, when the solution, on exposure to air, becomes oxidised into the green oxychloride, $CuCl_2(CuO)_3,4H_2O$.

534. Cupric Chloride, $CuCl_2$.—This chloride may be prepared by passing chlorine over copper, or dissolving either the carbonate or oxide in hydrochloric acid. On evaporation green crystals are formed, of the composition $CuCl_2,2H_2O$. The salt is deliquescent, and soluble in water. On being heated it loses half its chlorine, and is transformed into cuprous chloride.

535. Cuprous Iodide, Cu_2I_2.—This is the only known iodide of copper, and is precipitated by the addition of potassium iodide to cuprous sulphate, the latter salt being formed by heating cupric sulphate with sodium sulphite or other reducing agent. Cuprous iodide is insoluble in water, and is white, or yellowish-white, in colour. Iodine is sometimes separated in analysis by the formation of this iodide.

536. Cuprous Oxide, Cu_2O.—This compound occurs native as cuprite, crystallising in fine, ruby-red, octahedral crystals. It may be prepared by adding a large excess of sodium hydrate to a solution of cupric sulphate, and then sugar, till the precipitate dissolves with the formation of a blue solu-

tion. On gently heating, this throws down a red precipitate of cuprous oxide. Cuprous oxide is a stable body, which by solution in acids forms cuprous salts. A yellow precipitate of cuprous hydrate is afforded on treating cuprous chloride with caustic potash.

537. **Cupric Oxide, CuO.**—This oxide is obtained by heating either the nitrate or carbonate, when it occurs as a black powder. It is difficult when thus prepared to free the oxide from nitrous or carbon dioxide gases, and accordingly, for purposes where great purity is required, it is preferable to prepare the oxide by heating metallic copper in a current of air. The hydrate, $Cu(HO)_2$, is yielded as a light-blue precipitate on adding sodium hydrate to a solution of cupric sulphate; simply boiling the solution is sufficient to change the precipitate to the anhydrous black oxide. Ammonia dissolves cupric hydrate, with the formation of a deep blue-coloured liquid. Cupric oxide is dissolved by acids, forming green or blue cupric salts. It is at a red heat reduced to the metallic state either by hydrogen or carbon, and in consequence of this property is largely used in organic analysis. The substance under examination is mixed with a large excess of the oxide and raised to a red heat in a combustion-tube, copper is formed and the hydrogen and carbon of the substance are converted into water and carbon dioxide, which respectively are absorbed by calcium chloride and caustic potash. The oxide produced by roasting is best fitted for the purposes of analysis.

538. **Cupric Sulphide, CuS.**—This body may be formed by fusing together copper and sulphur; or, in the hydrated form, by passing sulphuretted hydrogen through a solution of some soluble copper salt.

Cuprous sulphide, Cu_2S, is formed when copper is heated in excess of sulphur.

On heating copper sulphides to a high temperature in the presence of air, sulphur dioxide is evolved, and copper oxide formed.

539. **Cupric Sulphate, $CuSO_4,5H_2O$.**—Copper sulphate may be obtained by roasting the sulphide at a very

gentle heat, and then lixiviating the mass. It is also formed when scrap copper is heated with strong sulphuric acid, when it separates out as a whitish substance, which, on treatment with water, yields a blue solution, from which fine crystals of copper sulphate, $CuSO_4,5H_2O$, separate. In the presence of ferrous sulphate the sulphate of copper becomes isomorphous with the iron compound and crystallises with it in crystals containing seven molecules of water. To remedy this, the mixed crystals are gently heated, when the ferrous sulphate decomposes before that of copper. The residue is treated with water, and copper sulphate recrystallised. Another plan consists of adding a small quantity of nitric acid, and thus converting the ferrous into ferric sulphate previous to crystallisation. On being heated to 100° copper sulphate loses four molecules of water of crystallisation, and at about 220° becomes anhydrous. In this form copper sulphate has a great attraction for water, and hence is used as a desiccating agent. Copper sulphate is employed in calico-printing, and in the preparation of Scheele's green (hydric cupric arsenite) and other pigments.

540. Cupric Nitrate, $Cu(NO_3)_2,6H_2O$.—This salt is produced by dissolving copper in nitric acid and evaporating, when the salt crystallises in blue crystals, which are deliquescent and very soluble in water. Cupric nitrate is a powerful oxidising agent, and is employed as such in various dyeing operations.

541. Carbonates of Copper.—The normal carbonate, $CuCO_3$, is unknown, but various basic carbonates may be precipitated by the addition of sodium carbonate to a solution of the sulphate. Malachite and chessylite are native basic copper carbonates.

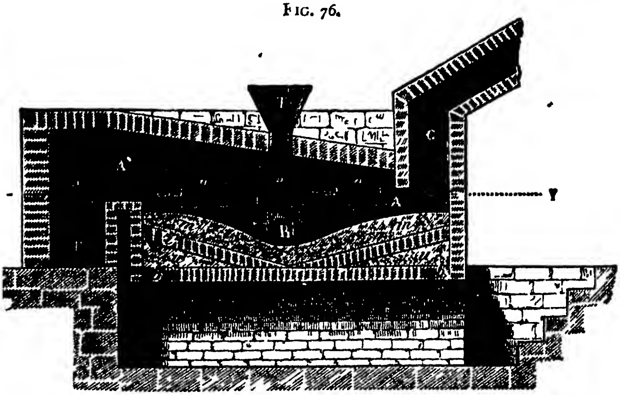
542. Other Salts of Copper.—Among these are included the bromides, which correspond to the chlorides. Copper also forms silicates, phosphates, and other salts. A number of double chlorides of copper and ammonium are known. The sulphate also forms similar compounds, among which is the deep blue liquid formed when ammonia is added in excess to copper sulphate solution; this compound consists of $CuSO_4(NH_3)_4H_2O$.

Lead.—Symbol, Pb. Atomic weight, 206·4.

543. **Occurrence.**—Lead occurs principally as the sulphide, galena, PbS. This mineral is highly crystalline, frequently occurring in almost perfect cubes and octahedra. It has a brilliant and metallic bluish lustre. Galena is found principally in England and Spain.

544. **Extraction.**—Lead is extracted from galena by heating it in a reverberatory furnace, after mixing with about a twentieth of its weight of lime. The furnace employed for this operation is shown in fig. 76, in which B represents a sloping

FIG. 76.



hearth, which is fed by the ore and flux through T. The fireplace is marked F, and the flue is shown at C. The ore is first heated somewhat gently in a strong current of air drawn through the furnace; by this means it is partly converted into the oxide and sulphate. This action having proceeded sufficiently far, the mass is raised in temperature, when the sulphide and sulphate with oxide mutually reduce each other, with the formation of metallic lead. This is removed from the furnace, and any siliceous gangue associated with the ore forms a slag with the lime. The various chemical reactions are shown in the following equations:—

$$\underset{\text{Lead sulphide.}}{2PbS} + \underset{\text{Oxygen.}}{3O_2} = \underset{\text{Lead oxide.}}{2PbO} + \underset{\text{Sulphur dioxide.}}{2SO_2}.$$

$$\underset{\text{Lead sulphide.}}{PbS} + \underset{\text{Oxygen.}}{2O_2} = \underset{\text{Lead sulphate.}}{PbSO_4}.$$

Then the mutual reactions of the three substances are represented in the following :—

$$\underset{\text{Lead sulphide.}}{PbS} + \underset{\text{Lead oxide.}}{2PbO} = \underset{\text{Lead.}}{3Pb} + \underset{\text{Sulphur dioxide.}}{SO_2}.$$

$$\underset{\text{Lead sulphide.}}{PbS} + \underset{\text{Lead sulphate.}}{PbSO_4} = \underset{\text{Lead.}}{2Pb} + \underset{\text{Sulphur dioxide.}}{2SO_2}.$$

The lead thus produced is freed from impurities by being melted and skimmed. The foreign metals are usually more oxidisable than the lead; the oxides thus formed rise to the surface and are removed.

Most galenas contain more or less silver, and for two reasons this should be removed from the lead; the first is that the silver injures the quality of the lead; the second is that silver possesses such a high commercial value as to make its extraction desirable. Quantities of silver, too small for profitable extraction otherwise, were first successfully removed from lead by what is known as Pattinson's process. This process depends on the general principle that alloys are more fusible than the metals of which they are composed. A number of melting-pans (some eight or nine) are arranged in series, and in the centre one of these a quantity of lead is melted and allowed to cool. On the solidifying point being reached crystals of lead separate; these are removed by a ladle, having a perforated bottom, and are deposited in the next pan on the right-hand side. When about four fifths of the lead have been thus removed, the remaining alloy, in which most of the silver is concentrated, is ladled into the left-hand pan. Another charge is introduced into the middle pan and undergoes the same operation. When the outer pots have become full, they are also melted and allowed to crystallise, the silver alloy always being transferred to the pan on the left, and the lead crystals to that on the right. In this way there accumulates in the pan on the extreme left an alloy containing as much as 300 ounces of silver to the ton, while that on the extreme right has its silver reduced to as little as half an ounce to the ton. The argenti-

ferous lead is worked for silver by a process to be described in the next chapter.

545. Properties.—Lead is a very soft metal, being capable of making a mark on paper, and can be cut with the nail. On being freshly cut lead has a bright bluish-white surface, which rapidly becomes tarnished through the formation of a film of oxide. This film acts as a protective coating, and prevents any further action on the metal. Lead is converted into oxide on being heated to a high temperature in air, but does not decompose water at any temperature. Sulphuric and hydrochloric acids are without action on lead at atmospheric temperatures, and only slightly attack the metal when boiled with it. Nitric acid readily dissolves lead, with production of nitrous fumes.

Although lead is so indifferent to the action of some of the very powerful acids, yet it is slowly dissolved in appreciable quantities by some very weak agents. Thus, pure air and pure water have no action on lead, but moist air slowly corrodes it. There is thus formed an oxide, which water removes by solution; this is precipitated as carbonate by atmospheric carbon dioxide, and a fresh portion of lead oxide is dissolved by the water. The corrosive action is accelerated by the presence of chlorides and nitrates in the water; sulphates and carbonates retard it, as they deposit a film of insoluble lead sulphate or carbonate on the surface of the metal and thus protect it from further action. In consequence of this action, soft waters which pass through lead pipes or are stored in lead cisterns, almost always show traces of lead in solution. The same danger does not exist with hard waters.

546. Industrial Applications.—The softness and ready fusibility of lead, combined with its comparative indifference to the action of many acids, leads to its employment for many purposes. Thus, sulphuric acid chambers and evaporating pans are formed of lead. Cisterns, pipes, and roofing are also formed of this material, rolled into sheets and then worked up into the required shape. The preparation of zinc sheets has caused these to more or less replace lead for roofing and certain

other purposes. Lead is used in the preparation of type-metal, pewter, and other alloys.

547. Plumbic Chloride, $PbCl_2$.—This substance is readily precipitated as a heavy white powder on adding hydrochloric acid to a solution of lead acetate or nitrate. The chloride is much more soluble in hot than in cold water, so that on heating the chloride with water it dissolves and is re-precipitated as the liquid cools. Lead chloride fuses on being heated, and on cooling solidifies into a horny mass.

Several oxychlorides of lead are known, of which $PbCl$, $PbCl_2$ is the most important.

548. Plumbic Oxide, PbO.—This body is known commercially as litharge, and is manufactured by the oxidation of lead in a current of air. Prepared in this manner it forms a yellow powder which readily fuses at a full red heat. The hydrate, $Pb(HO)_2$, is formed when lead nitrate is precipitated by sodium hydrate. Lead oxide is slightly soluble in water, to which it imparts an alkaline reaction, being a very strong base. It readily absorbs carbon dioxide, with the formation of a carbonate.

549. Red Lead, Pb_3O_4.—Red lead is a body of somewhat variable composition, it being composed of plumbic oxide, PbO, combined in various proportions with the dioxide, PbO_2. The most usual combination is represented by $(PbO)_2,PbO_2$, a formula equivalent to Pb_3O_4. To prepare this body, litharge, finely powdered, is heated to a temperature of 320° C. on trays placed in a reverberatory furnace; oxygen is absorbed and this compound formed. This body, called also minium, is of a fine red colour, and is largely used in the manufacture of flint glass. At a high temperature minium is decomposed into plumbic oxide with evolution of oxygen.

550. Plumbic Dioxide, PbO_2.—This compound, called also the peroxide and puce-coloured oxide of lead, is prepared by treating minium with boiling nitric acid, when that compound is decomposed :—

$$\underset{\text{Minium.}}{(PbO)_2PbO_2} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Lead nitrate.}}{2Pb(NO_3)_2} + \underset{\text{Lead peroxide.}}{PbO_2}.$$

The residual peroxide is washed first with nitric acid and subsequently with water, and afterwards dried. Lead peroxide is insoluble in water and most acids, but dissolves on fusion with potassium hydrate. In this reaction, potassium plumbate, K_2PbO_3 is formed, so that the peroxide has feebly acid properties. On being heated it evolves oxygen with the formation of litharge. On heating together hydrochloric acid and the peroxide, plumbic chloride is produced and chlorine liberated.

551. **Plumbic Sulphide, PbS.**—This constitutes the mineral galena; the sulphide is also formed on fusing sulphur and lead together, and in the wet way by precipitating a soluble lead salt with sulphuretted hydrogen. The behaviour of galena when heated in the presence of air has already been explained. Galena may also be reduced by fusion with metallic iron, when iron sulphide, and metallic lead are produced. Nitric acid dissolves the sulphide, with the separation at first of free sulphur. Hot hydrochloric acid attacks it, with the formation of the chloride and evolution of free sulphuretted hydrogen.

552. **Plumbic Sulphate, $PbSO_4$.**—This salt is produced by the addition of sulphuric acid to a solution of lead nitrate. It is insoluble in water, slightly soluble in nitric acid, and readily soluble in a solution of ammonium acetate. The sulphate requires a high temperature for its decomposition when heated alone, but in the reducing flame of the blowpipe. is readily converted into metallic lead.

553. **Plumbic Nitrate, $Pb(NO_3)_2$.** — By dissolving litharge in dilute nitric acid, and evaporating the solution, anhydrous crystals of this salt separate. Lead nitrate is soluble in water, but only slightly soluble in nitric acid. On being heated the salt decrepitates strongly and evolves nitrogen peroxide and oxygen, leaving a residue of plumbic oxide. Lead also forms a basic nitrate.

554. **Carbonates of Lead.**—The normal carbonate, $PbCO_3$, occurs as a mineral, commonly associated with galena. Lead carbonate, when ground, constitutes the well-known pigment, white lead, and is prepared in large quantities. The

readiness with which lead carbonate is formed shows what an energetic base lead oxide is. For use in the fabrication of paint, white lead manufactured by the 'Dutch' method is preferred, as it possesses greater opacity and covering power. The following is an outline of this method: Thin sheet lead is made up into rolls, each of which is placed on end in an earthenware pot, which is about one-quarter filled with weak vinegar (dilute acetic acid). The pots are loosely covered, arranged in rows, and then embedded in tan or horse-dung. The heat of decomposition of the organic manure evaporates the vinegar, which attacks the lead, forming an acetate. The carbon dioxide evolved from the tan converts this into carbonate, with the liberation of acetic acid, which attacks a fresh portion of lead. In this way, a small quantity of vinegar suffices for the production of a considerable amount of lead carbonate. The operation of conversion occupies from four to five weeks. White lead prepared in this manner has a variable composition, but usually consists of $(PbCO_3)_2Pb(HO)_2$.

On being heated lead carbonate is decomposed into carbon dioxide and plumbic oxide. The salt is insoluble in pure water, but dissolves in water containing carbonic acid. In common with all other lead compounds it is blackened by the action of sulphuretted hydrogen.

555. **Other Salts of Lead.**—Lead forms a bromide and iodide. The latter, PbI_2, is a yellow body precipitated from a solution of lead nitrate by the action of potassium iodide. Like the chloride it is much more soluble in hot than in cold water. It therefore dissolves in water when heated with it; this solution deposits yellow lustrous crystals on cooling. Lead forms phosphates with each modification of that acid, these phosphates being utilised in the preparation of the acids themselves. Lead silicate forms an important constituent of flint glass.

CHAPTER XXVIII

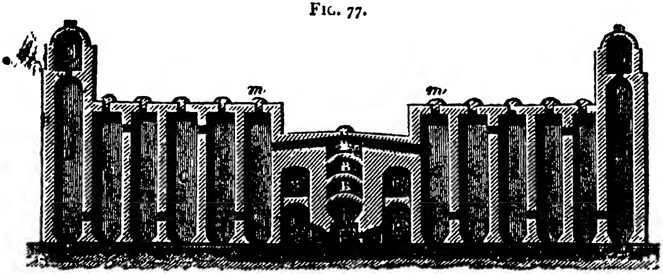
THE NOBLE METALS

Mercury.—Symbol, Hg. Atomic weight, 199·8. Observed vapour-density, 100·66. Molecular weight, 199·8. Melting-point, −39·8°. Boiling-point, 357° C.

556. **Occurrence.**—Small quantities of mercury are found native; but the most common ore is the sulphide, HgS, known also as cinnabar. This is found and worked in Spain, Idria, and California, and also in other localities.

557. **Extraction.**—The ores of mercury are easily reduced, either by roasting in a current of air, when the sulphur is oxi-

FIG. 77.



dised, leaving the metal to be distilled in the free state, or by the use of some reducing agent, which combines with the sulphur. For this latter purpose lime is frequently employed. Fig. 77 is an illustration of the furnace and condensing chambers used in Idria for mercury-extraction. The fireplace is marked A, while on either side, and marked G H, are chambers by which air is admitted. The ore is arranged in the spaces B B B, and through these pass the products of combustion of the fire, accompanied by an excess of air. Sulphur dioxide, together with mercury vapour, pass over, the latter being condensed within the chambers C C. The end chambers, D D, are so arranged that the last portions of mercury vapour are con-

densed by a falling stream of water. The liquid mercury is drawn off from the bottom of these chambers, filtered through cloth, and stored in wrought-iron bottles.

Traces of zinc and other metals are found in mercury as thus prepared; from these mercury may be purified by exposure in shallow vessels to nitric acid or a solution of mercurous nitrate. The impurities are dissolved, and when the mercury salt is used their equivalent of mercury is deposited in the free state. The most effectual method of purifying the metal is by carefully-conducted redistillation.

558. **Properties.**—Mercury is distinguished from other metals by its property of becoming liquid at ordinary temperatures. The metal is silver-white, and its surface, when pure, forms a most perfect and lustrous mirror. In pure air mercury is unaltered, but tarnishes in the presence of sulphuretted hydrogen. The purity of the metal may be judged by its comparative mobility; in the pure state, drops of mercury are almost perfectly spherical and run with remarkable speed; impurities cause the drop to run more slowly, leaving behind a tail or streak of semi-liquid metallic matter. The metal solidifies at a temperature of $-39{\cdot}8°$, and is then malleable, having a hardness about equal to that of tin. Mercury is volatile at all temperatures from $-41°$ upwards, and boils at $357°$, with the production of a colourless vapour. The density of mercury vapour shows that the molecule of this metal is monatomic. As was explained in the chapter on oxygen, mercury, at a temperature near its boiling-point, combines with oxygen to form mercuric oxide, HgO, which oxide is again decomposed at a higher temperature. Chlorine, bromine, iodine, and sulphur, all combine directly with mercury at ordinary temperatures. Hydrochloric acid is without action on mercury, but hydriodic acid, although usually weaker in action, dissolves the metal slowly, with evolution of hydrogen; so also does sulphuretted hydrogen. Mercury forms, when heated with concentrated sulphuric acid, mercurous sulphate, Hg_2SO_4, with the liberation of sulphur dioxide. Nitric acid readily dissolves the metal, forming either mercurous or mer-

curic nitrate, according to whether the mercury or acid is in excess.

Mercury readily combines with most of the metals, even at ordinary temperatures, with the formation of alloys, which are known as 'amalgams.' Light and heat are evolved when mercury thus combines with sodium and potassium; the amalgams produced are hard and brittle. Gold and silver form amalgams with readiness; iron and platinum only with difficulty.

559. Industrial Applications.—Metallic mercury is employed in medicine and the preparation of the various mercury compounds. It is also used in the preparation of barometers, other scientific instruments, and in the laboratory for filling various forms of apparatus in which gases are manipulated. The fact that mercury neither dissolves nor has other action on most gases, renders it exceedingly valuable for this latter purpose. Mercury is largely used in the extraction of gold and silver from their ores, and also in the preparation of tin amalgam as a backing for glass mirrors.

560. Salts of Mercury.—Of these there are two series, in one of which mercury acts as a dyad, forming salts corresponding to the cupric salts. In the other series, mercury functions as a monad, and yields mercurous salts, of which mercurous chloride, Hg_2Cl_2, is an example.

561. Mercurous Chloride, Hg_2Cl_2.—This body, called also calomel, is obtained by heating together in the proper proportions mercuric chloride and mercury, when calomel is formed as the mixture condenses—

$$\underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Mercury.}}{Hg} = \underset{\text{Mercurous chloride.}}{Hg_2Cl_2}.$$

The salt may also be obtained by adding hydrochloric acid to a solution of mercurous nitrate, when a heavy white precipitate is produced. Calomel is volatile at temperatures below a red heat, and forms a colourless vapour, whose density is only half that required by the formula Hg_2Cl_2. In consequence, it has been proposed to assign it the formula HgCl. There is evidence, however, that the vapour of mercurous chloride

contains free mercury, as it amalgamates a cold gold surface exposed to its action. The presumption is that in the vaporous state the molecule of mercurous chloride, Hg_2Cl_2, is dissociated into a molecule of mercuric chloride, $HgCl_2$, and one of mercury, Hg. Such a decomposition would account for the difference in vapour-density. There are, however, certain difficulties in the way of this explanation, which lead some chemists to still look with favour on the expression HgCl for the gaseous molecule. The dissociation hypothesis is supported by the behaviour of mercurous oxide when subjected to heat. Mercurous chloride is insoluble in water, and is blackened by a solution of ammonia, forming a compound represented by the formula $NH_2Hg'_2Cl$.

$$\underset{\text{Mercurous chloride.}}{Hg_2Cl_2} + \underset{\text{Ammonium hydrate.}}{2NH_4HO} = \underset{\text{Dimercurous ammonium chloride.}}{NH_2Hg'_2Cl} + \underset{\text{Ammonium chloride.}}{NH_4Cl} + \underset{\text{Water.}}{2H_2O.}$$

Dimercurous ammonium chloride may be viewed as ammonium chloride in which two atoms of hydrogen have been replaced by two atoms of monad mercury. Calomel is largely used in medicine.

562. Mercuric Chloride, $HgCl_2$.—Mercuric chloride may be prepared by heating mercury in an atmosphere of chlorine, or preferably by subliming mercuric sulphate together with common salt—

$$\underset{\text{Mercuric sulphate.}}{HgSO_4} + \underset{\text{Sodium chloride.}}{2NaCl} = \underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Sodium sulphate.}}{Na_2SO_4.}$$

The mercuric chloride, called also corrosive sublimate, condenses in long crystalline needles. The salt, on being heated, fuses, and boils at a temperature of 295°; the vapour has a density agreeing with that of the formula $HgCl_2$. Mercuric chloride is soluble in water, and when to this solution ammonia is added the following change occurs:—

$$\underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Ammonium hydrate.}}{2NH_4HO} = \underset{\text{Mercuric ammonium chloride.}}{NH_2Hg''Cl} + \underset{\text{Ammonium chloride.}}{NH_4Cl} + \underset{\text{Water.}}{2H_2O.}$$

The mercuric ammonium chloride is deposited as a *white precipitate*, by which name it is commonly known. It is very

similar in constitution to the mercurous compound formed in a similar manner, only in this case two atoms of hydrogen are replaced by one atom of dyad mercury. Mercuric chloride and ammonia form a somewhat extensive series of what may be called substitution ammonium products; these are of considerable interest in connection with the whole subject of the replacement of hydrogen atoms in the ammonia and ammonium molecules. Mercuric chloride, in very small quantities, coagulates albumin compounds. It is a very violent poison, and the most powerful antiseptic with which we are acquainted.

563. **Mercurous Oxide, Hg_2O.**—This body may be obtained by treating calomel with a solution of sodium hydrate and washing the black precipitate thus formed. On being heated it readily decomposes into the metal and mercuric oxide.

564. **Mercuric Oxide, HgO.**—The production of this oxide by heating mercury in air is of theoretic interest; but a far more convenient mode of preparation is by heating mercuric nitrate, when a red crystalline form of the oxide remains. The oxide may also be prepared in the wet way, by adding sodium hydrate to a solution of mercuric chloride, when the oxide is precipitated as a *yellow* powder, having the same composition as the red form. The precipitated oxide is much more active, chemically, than the red variety. On application of heat, the oxide is decomposed into mercury and free oxygen.

Both mercurous and mercuric oxides are active basic bodies.

565. **Mercuric Sulphide, HgS.**—This compound occurs naturally as the mineral cinnabar, and may also be prepared artificially by heating together mercury and sulphur in closed vessels, and allowing the sulphide to condense on the cold lid. Prepared in this manner mercuric sulphide is of a brilliant red colour, and constitutes the well-known pigment, vermilion. Sulphuretted hydrogen precipitates mercuric sulphide in a black powder when passed through a solution of mercuric chloride; this becomes red on sublimation in vessels from which air is excluded. On being heated in air, the sul-

phide is decomposed, with production of sulphur dioxide and metallic mercury.

566. **Mercuric Sulphate, $HgSO_4$.**—This body is formed when mercury is heated with concentrated sulphuric acid, sulphur dioxide being evolved. At first the mercurous sulphate, Hg_2SO_4, is formed, but this is decomposed as the temperature increases. Mercuric sulphate is a white powder, only very slightly soluble in water, being decomposed, with the formation of an insoluble yellow basic sulphate, Hg_3SO_6.

567. **Mercurous Nitrate, $Hg'_2(NO_3)_2$.**—This salt is formed when dilute nitric acid acts in the cold on excess of mercury. It forms white, somewhat efflorescent, and soluble crystals. A number of basic mercurous nitrates can also be formed.

568. **Mercuric Nitrate, $2Hg''(NO_3)_2,H_2O$.**—When mercury is dissolved in excess of nitric acid, this compound is formed. Like the mercurous salt, a large number of basic mercuric nitrates are also known.

569. **Other Salts of Mercury.**—Among these the bromides may be mentioned as resembling the chlorides in properties.

Mercuric Iodide, HgI_2, may be prepared by subliming a mixture of mercury and iodine, or in the wet way by precipitating mercury chloride with a solution of potassium iodide. Mercuric iodide is a brilliant red powder, which on being gently heated is changed into a yellow variety; simple friction reconverts the yellow into the red form of the salt.

Mercurous carbonate, Hg_2CO_3, and various basic mercuric carbonates are known.

Neither borates nor silicates of mercury have as yet been prepared.

Silver.—Symbol, Ag. Atomic weight, 107·66.

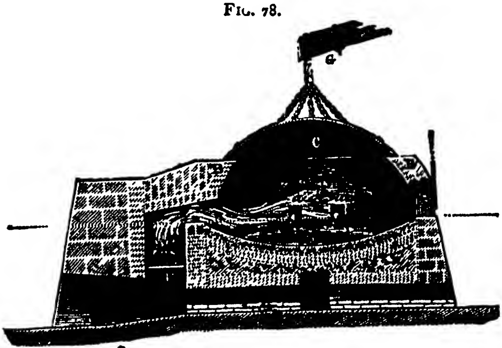
570. **Occurrence.**—Silver occurs in nature in the free state, and also as sulphide, either pure or in combination with galena. Extensive silver mines exist in various parts of both North and South America.

571. Extraction.—Silver in the metallic state is extracted from its ores either by dissolving it in mercury (amalgamation) or fusing the ore with lead and thus obtaining an alloy of lead. The sulphide ores are also worked by amalgamation processes. The ore is in the first place roasted with common salt, by which the silver is converted into chloride. The silver chloride is next agitated in casks together with scrap-iron and mercury; the iron deposits the silver in the metallic state, when it is dissolved by the mercury.

The liquid silver amalgam is filtered through canvas bags, when the excess of mercury is forced out and a pasty amalgam remains. This is heated to expel the mercury, and the spongy mass of remaining silver is fused and cast into ingots.

The silver-lead alloy produced when lead is used as the extracting agent for silver, and also that obtained by Pattinson's desilverising process for lead, are subjected to an operation termed *cupellation*, in order to produce metallic silver. In fig. 78

Fig. 78.



an illustration of the German cupellation-furnace is given. The hearth of the furnace A, is hollow, and is lined with a mixture of clay and lime (natural marl). On this is placed the argentiferous lead. A brisk current of air is drawn through the fireplace F, and thus the metal is melted in the presence of a powerful oxidising flame. The lead is oxidised to litharge, which partly runs out of the furnace through a channel prepared for that purpose, and is partly absorbed in the materials with

which the hearth is lined. After the oxidation of the whole of the lead a brilliant mass of fused silver remains on the hearth.

Silver is at times extracted from its ores in the wet way. On gently roasting, the sulphide, together with those of copper and iron, is oxidised into sulphate. The heat is then raised sufficiently to decompose the iron and copper salts; after which silver sulphate is extracted by lixiviation with hot water. The silver is also sometimes extracted from the ore when in the form of chloride by solution in sodium thiosulphate.

572. Properties.—Silver is an almost purely white metal, capable of taking a very high polish, which in pure air it retains indefinitely. The metal can be drawn into fine wire or hammered into very thin foil. It is when pure the best conductor of heat and electricity known. Silver melts at 916°, and in the oxyhydrogen blowpipe flame can be distilled. Melting silver possesses the property of mechanically dissolving oxygen to the extent of over twenty times its volume. As the metal cools, this oxygen is again expelled unchanged. Chlorine, bromine, iodine, and sulphur combine directly with silver. The presence of sulphuretted hydrogen in the atmosphere causes the tarnishing of metallic silver, which rapidly becomes black. Hydrochloric acid acts on silver very slightly, but hydriodic acid attacks it, with evolution of hydrogen. At its boiling-point, sulphuric acid combines with silver to form silver sulphate, sulphur dioxide being evolved. Nitric acid dissolves silver with readiness. The fused caustic alkalies have little action on silver, hence they are concentrated by fusion in silver vessels when required in a pure form.

573. Industrial Applications.—Silver is largely used for purposes of coinage, and also in the manufacture of articles of silver plate. In the pure state it is too soft to be employed to advantage for these purposes, so it is alloyed with from 7 to 10 per cent. of copper. Many articles are simply coated with silver, and are then known commercially as electro-plate, the silver coating having been deposited by means of an electric current.

574. Argentic Chloride, AgCl.—This body occurs native, when it is known as horn silver, from its peculiar horny appearance when melted. On the addition of hydrochloric acid, or a soluble chloride, to a silver salt in solution, a white curdy precipitate of this chloride is deposited. Silver chloride is insoluble in water and dilute acids, but is readily dissolved by ammonia. Potassium cyanide and sodium thiosulphate also readily dissolve this salt. When subjected to the action of light, silver chloride becomes darkened in colour, owing to the formation of a sub-chloride (Ag_4Cl_3?) and the liberation of chlorine. Silver chloride readily melts, and may be reduced to the metallic state by simple contact with zinc or iron.

575. Argentic Oxide, Ag_2O.—On adding a solution of sodium hydrate to argentic nitrate solution, a brown precipitate of silver oxide is formed. This body is readily reduced by the action of light or hydrogen, or even heat alone, to the metallic state. It is slightly soluble in water, to which it imparts an alkaline reaction, and is a powerful base, forming salts which are usually anhydrous and isomorphous with those of sodium, with which metal it is associated in the grouping effected by application of the periodic law.

A peroxide of silver (Ag_2O_2?) appears as long, needle-like crystals on the same electrode as the metallic silver when argentic nitrate is decomposed by an electric current.

576. Argentic Sulphide, Ag_2S.—This body occurs native as the most important of the silver ores. It is readily formed by direct combination of sulphur and silver with each other. Silver sulphide is thrown down as a black precipitate when sulphuretted hydrogen is passed through a solution of the nitrate. When roasted in air the sulphide is gradually reduced to the metallic state, a portion being also converted into the sulphate.

577. Argentic Sulphate, Ag_2SO_4.—This body, as just mentioned, is produced in the roasting of silver sulphide, and is also formed when silver is dissolved in boiling sulphuric acid. The addition of water causes the salt to be precipitated, as 88 parts of water dissolve only one part of silver sulphate.

It crystallises in prisms isomorphous with those of anhydrous sodium sulphate.

578. **Argentic Nitrate, $AgNO_3$.** — Silver nitrate is readily prepared by the solution of pure silver in nitric acid and water in equal parts. On evaporation, square, colourless, tabular crystals separate. These are anhydrous, non-deliquescent, and soluble in water. To obtain silver nitrate from solution of an alloy of silver and copper, a portion of the solution is treated with potassium hydrate; this precipitates silver oxide, together with a small portion of copper oxide. This is washed, and then boiled with the remainder of the solution, when any copper nitrate present is precipitated as copper oxide, and an equivalent of silver dissolved in its place. Silver nitrate readily melts, and when cast into sticks forms the lunar caustic of the surgeon. With greater application of heat, silver nitrate is decomposed into the oxides of silver and nitrogen, the former of which, on being yet further heated, is resolved into metallic silver and oxygen. Light has no action on pure silver nitrate, but in the presence of organic matter blackens it, thus forming a permanent stain, which is unremovable by soap and water.

579. **Other Salts of Silver.**—Principal among these are the bromide and iodide, which are prepared by precipitating silver nitrate respectively with potassium bromide or iodide. They are insoluble in water, and, like the chloride, are affected by the action of light. This property leads to their being employed as the basis of the sensitive plates used in photography. Silver bromide, AgBr, is difficultly soluble in ammonia, while the iodide, AgI, is practically insoluble. Silver fluoride, AgF, is obtained by dissolving silver oxide in hydrofluoric acid; it is a very soluble deliquescent salt. Silver carbonate, Ag_2CO_3, may be prepared by precipitating argentic nitrate solution with sodium carbonate.

Gold.—Symbol, Au. Atomic weight, 196·2.

580. **Occurrence.**—Gold mostly occurs in the free state, either in alluvial deposits, known as stream gold, or in quartz

veins (auriferous quartz). Gold deposits are found in small quantities in Cornwall, Wales, and Scotland; but the principal goldfields of the world are those of Australia and California. Gold is also found in the Ural Mountains, and various other parts of Asia, as well as in Africa.

581. **Extraction.**—Alluvial gold is extracted by a very simple process; the clay or gravel in which it is contained is carefully washed, when the lighter materials float away, and the heavy gold remains. At times the metal occurs in nuggets of considerable size. The ore from the gold-bearing quartz formations is crushed to a fine powder, and then the gold extracted by amalgamation. Native gold is always more or less alloyed with silver, from which it is purified by solution in aqua regia, and precipitation of the silver by hydrochloric acid. The auric chloride is reduced by the addition of ferrous sulphate solution, when gold is deposited as a fine powder. This is collected and fused into ingots, under borax.

582. **Properties.**—Gold is a soft metal of a fine yellow colour, and capable of taking a very high polish It is absolutely unaffected by air at all temperatures. Gold is the most malleable of metals, and by hammering is reduced to gold-leaf of not more than $\frac{1}{280000}$ of an inch in thickness. Gold-leaf still retains its metallic appearance, and reflects yellow light; but it also transmits light of a greenish colour. When still thinner, the metallic lustre disappears, and the transmitted light is of a ruby colour. Gold melts at 1037°, and is scarcely volatile at the highest furnace heats; it is one of the best conductors of heat and electricity. The only single acid that has any effect on gold is selenic acid, by which it is dissolved; nitric, hydrochloric, and sulphuric acids are absolutely without effect on it. [Very finely divided gold is stated, on the authority of Boland, to dissolve slowly in hydrochloric acid.] Aqua regia, or any acid liquid evolving chlorine, dissolves the metal, with formation of the chloride. The caustic alkalies are without action on gold, but chlorine, bromine, and fluorine combine directly with it.

583. **Industrial Applications.**—Gold is used in the

manufacture of coinage; also in that of jewellery and plate. For these purposes it is alloyed with copper or silver, in order to increase its hardness. In the form of gold-leaf it is employed to gild wood and other substances; articles are also coated with gold by a process of electro-plating. Bohemian ruby glass is coloured by gold in an extremely fine state of division.

584. **Auric Chloride, $AuCl_3$.**—This salt is prepared by dissolving gold in aqua regia, employing an excess of hydrochloric acid; finally, the solution is treated with hydrochloric acid alone, and concentrated over the water bath so as to expel all nitric acid. On careful evaporation to dryness, the salt is obtained in a deliquescent form. A slight elevation of temperature causes its decomposition into very slightly soluble aurous chloride, AuCl, and free chlorine. Further heat drives off the whole of the chlorine, leaving metallic gold. Auric chloride dissolves in water, forming a rich yellow solution, from which gold is easily precipitated by reducing agents. Among these may be mentioned, ferrous sulphate, sulphur dioxide, oxalic acid, phosphorus, and several of the metals.

585. **Auric Oxide, Au_2O_3.**—By adding magnesia to a solution of auric chloride, a precipitate of the oxide is formed. This is washed and separated from the magnesia by treatment with dilute nitric acid, which dissolves the latter, leaving behind a yellow powder, which is the hydrated oxide, $Au(HO)_3$. Very gentle heating renders this anhydrous. Auric oxide may be reduced to the metallic state by the action of light, or elevation of temperature to 245°. Auric oxide dissolves in hydrochloric acid, with the formation of the chloride. The hydrate, sometimes called auric acid, dissolves in solution of the alkaline hydrates, forming compounds termed aurates.

586. **Auric Sulphide, Au_2S_3.**—This body may be precipitated as a yellow precipitate by passing sulphuretted hydrogen through a solution of auric chloride.

587. **Other Salts of Gold.**—The bromides and iodides correspond in composition to the chlorides. Purple of Cassius

is the name given to a purple precipitate obtained by adding a mixture of stannous and stannic chlorides to a solution of auric chloride. It is probably a double stannate of gold and tin. Purple of Cassius is employed as a pigment in china-painting, producing a tint varying from pale pink to a rich rose red.

Platinum.—Symbol, Pt. Atomic weight, 196·7.

588. **Occurrence.**—Platinum is always found in nature in the uncombined state, but is usually associated with iridium, and other of what are called the platinum metals. The metal is found in alluvial deposits in the Ural Mountains, and also in Mexico, California, and Australia.

589. **Extraction.**—Platinum is extracted from its ores by treatment with aqua regia, by which the metal and others of the platinum group are dissolved. This solution is evaporated to dryness and heated sufficiently to decompose the chlorides of palladium and iridium, which are thus rendered insoluble. The platinum chloride is taken up with water, and precipitated by the addition of ammonium chloride. This precipitate is washed, dried, and heated to redness, when a spongy mass of metallic platinum remains. This was formerly subjected to the action of a press, and then forged and welded at a white heat into an ingot of platinum. At present the spongy platinum is usually fused in the oxy-hydrogen furnace, in the manner described and illustrated (fig. 11) in the chapter on Hydrogen.

590. **Properties.**—Platinum is a malleable and ductile white metal of about the hardness of copper. It has a specific gravity of 21·5 and is the heaviest substance known (excepting osmium and iridium.) Platinum is fusible only at the highest temperatures at our command, requiring for that purpose the heat of the oxyhydrogen blowpipe or voltaic current. Platinum does not directly combine with oxygen at any temperature, neither is it affected, when pure, by any single acid. Aqua regia dissolves it, although slowly. The caustic alkalies attack platinum much more readily than they do gold or silver. Chlorine in the dry state does not attack platinum.

On heating the double chloride of platinum with ammonium,

Am_2PtCl_6, it is decomposed, with the liberation of metallic platinum in a very finely divided state. In this condition platinum exhibits a remarkable capacity for condensing various gases within its pores. Spongy platinum, or platinum black as this body is termed, according to its degree of fineness, absorbs oxygen from the atmosphere, and when held in the vapour evolved from ether or alcohol, glows with the heat produced by the union of these with the condensed oxygen. A jet of hydrogen impinging against such spongy platinum is inflamed.

Platinum somewhat readily forms alloys with the more fusible metals, and so such metals or their reducible compounds cannot be heated in vessels of platinum.

591. **Industrial Applications.**—Platinum is used in the manufacture of crucibles, dishes, and other pieces of chemical apparatus. The stills employed for the concentration of sulphuric acid are also constructed of this metal.

592. **Platinic Chloride, $PtCl_4$.**—This salt is prepared by dissolving platinum in aqua regia and evaporating the solution to dryness over a water bath. Platinum chloride on being heated to 235° is decomposed into platinous chloride, $PtCl_2$, with evolution of chlorine. Further application of heat reduces the platinous chloride to metallic platinum. Platinic chloride is soluble in water, and is characterised by the production of insoluble double salts, with potassium and ammonium, having the respective formulæ K_2PtCl_6 and Am_2PtCl_6. These salts are used in the quantitative estimation of these bodies.

593. **Platinic Oxide, PtO_2.**—This compound is obtained by gently heating the corresponding hydrate, $Pt(HO)_4$; this latter is produced by precipitating platinic chloride with potassium hydrate. A double salt is formed, and from this the potash is dissolved by digestion with acetic acid; it is thus obtained as an almost white precipitate. Platinic hydrate functions toward strong bases as a weak acid; sodium platinate has been prepared in the crystalline form. The oxide dissolves in hydrochloric and other acids, with the formation of the corresponding salts.

594. Other Compounds of Platinum.—Platinum forms a lower oxide, PtO, corresponding to platinous chloride. It also forms bromides and iodides. A sulphate and nitrate of platinum are known. Platinum forms two sulphides, PtS and PtS_2, corresponding to the oxides. Platinum forms a peculiar series of substitution salts with ammonium compounds, resembling in character the mercur-ammoniums. Some interesting salts of platinum termed platonitrites are also known, of which potassic platonitrite, $K_2(NO_2)_4Pt$, is an example.

APPENDIX

METRIC WEIGHTS AND MEASURES

FOR the complicated system of weights and measures in use in England, most chemists substitute the very simple metric system. The unit of the system is the mètre, a rod of platinum deposited in the archives of France, which, when constructed, was supposed to be one-ten-millionth part of the quadrant of a great circle encompassing the earth on the meridian of Paris.

Measures of Length.—The mètre measures 39·37 inches. It is multiplied and subdivided by 10 for the higher and lower measures of length.

				Inches
Kilomètre	= 1000 mètres		=	39370
Hectomètre	= 100	,,	=	3937·0
Decamètre	= 10	,,	=	393·70
Mètre			=	39·370
Decimètre	= 0·1	mètre	=	3·9370
Centimètre	= 0·01	,,	=	0·39370
Millimètre	= 0·001	,,	=	0·03937

The Greek prefixes deca, hecto, and kilo are used to represent 10, 100, and 1000 respectively; and the Latin deci, centi, and milli signify a tenth, hundredth, and thousandth.

The prefixes are used with the same meaning in the other measures. The decimètre is very nearly 4 inches in length: this affords an easy method of roughly translating measures of the one denomination into those of the other.

Measures of Capacity.—The measure of capacity is derived from that of length by taking one cubic decimètre as the unit:

this is named the litre, the capacity of which and that of its derivatives in English measures are appended :—

				Cubic inches	Pint
Kilolitre	= 1000	litres	=	61027	1760·7
Hectolitre	= 100	,,	=	6102·7	176·07
Decalitre	= 10	,,	=	610·27	17·607
Litre			=	61·027	1·7607
Decilitre	= 0·1	litre	=	6·1027	0·17607
Centilitre	= 0·01	,,	=	0·61027	0·017607
Millilitre	= 0·001	,,	=	0·06102	0·0017607

The litre, being the capacity of a cubic decimètre, it is evident that the millilitre equals in volume a *cubic centimètre* ; this latter term, or its abbreviation (c.c.) is very frequently used in preference to millilitre ; thus a pipette is said to contain 50 c.c., and a litre flask is often called a 1000 c.c. flask.

A cubic inch is equal to 16·38 cubic centimètres.

Measures of Weight.—The weight of one cubic centimètre of distilled water at its maximum density (4° C.) is taken as the unit of weight, and is called a gramme or gram. The subdivisions and multiples are again the same :—

				Grains	Avoirdupois ounces
Kilogram	= 1000	grams	=	15432·3	35·2739
Hectogram	= 100	,,	=	1543·23	3·527·9
Decagram	= 10	,,	=	154·323	0·352739
Gram			=	15·4323	0·0352739
Decigram	= 0·1	gram	=	1·5432	0·003527
Centigram	= 0·01	,,	=	0·15432	0·0003527
Milligram	= 0·001	,,	=	0·015432	0·00003527

A kilogram is a little over 2 lbs. 3¼ oz., and a hectogram 3½ oz. An ounce avoirdupois equals 28·35 grams.

The relation between the weight and volume of water is seen to be a very simple one; the volume being the same number of c.c. as the weight is grams. With other liquids the volume in c.c. × specific gravity = weight in grams.

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